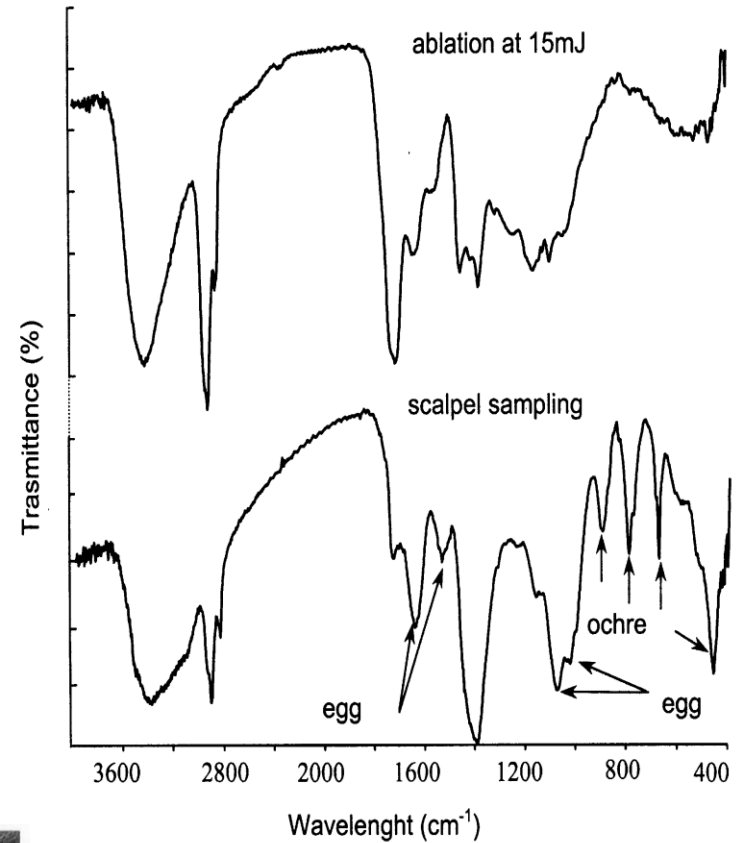


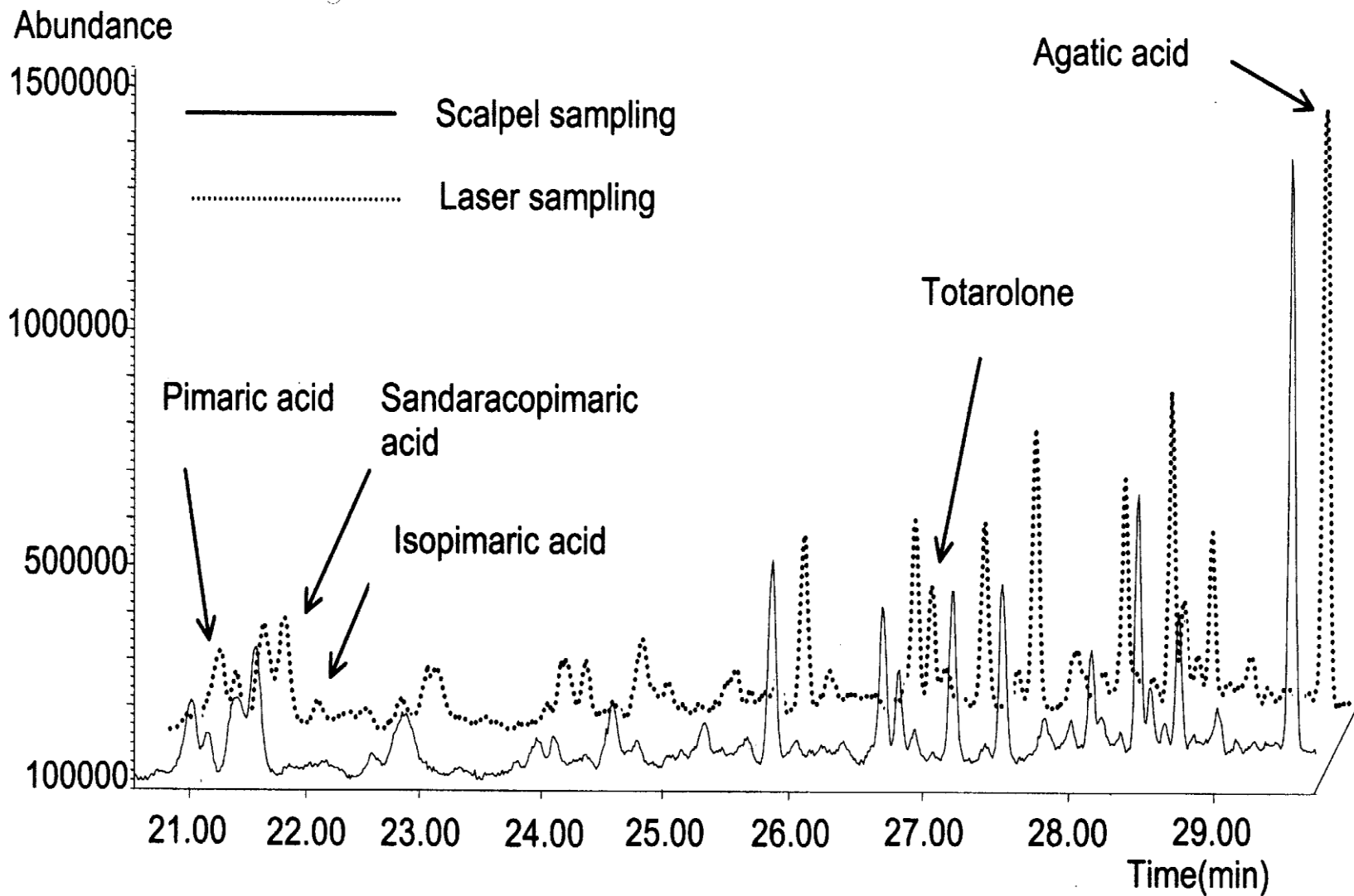
# **Analytické aplikace laserů**

# Vzorkování maleb laserovým paprskem

Er:YAG laser



FTIR spektra ablatovaného materiálu při energii laseru 15 mJ a vzorku odebraného skalpelem.



Chromatogramy vzorku odebraných skalpelem (—) a laserem (.....).

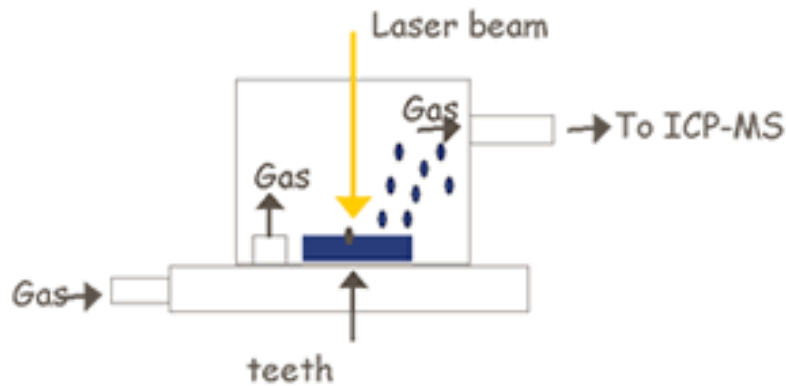
# LA-ICP-MS

LA-ICP-MS method

Laser beam → surface of teeth

Small amount of mass → vaporized

Vaporized particles → ICP-MS



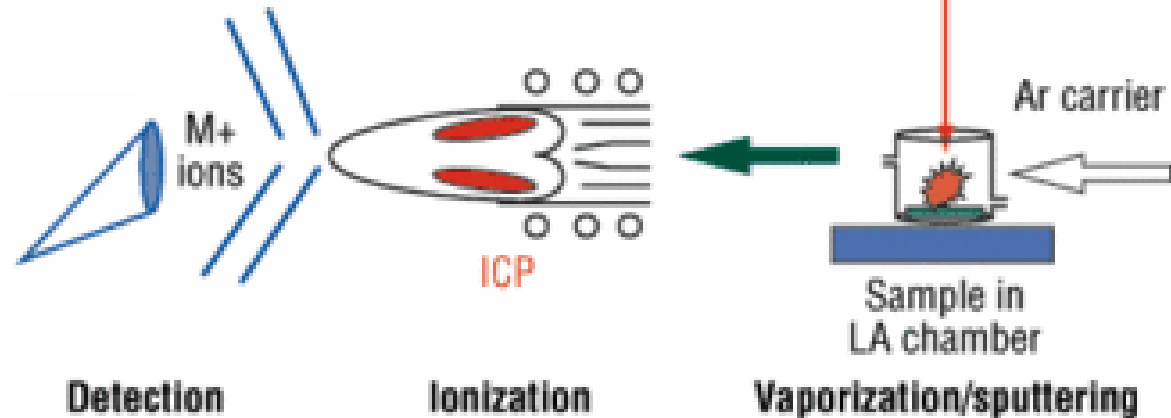
Nd:YAG

Excimer

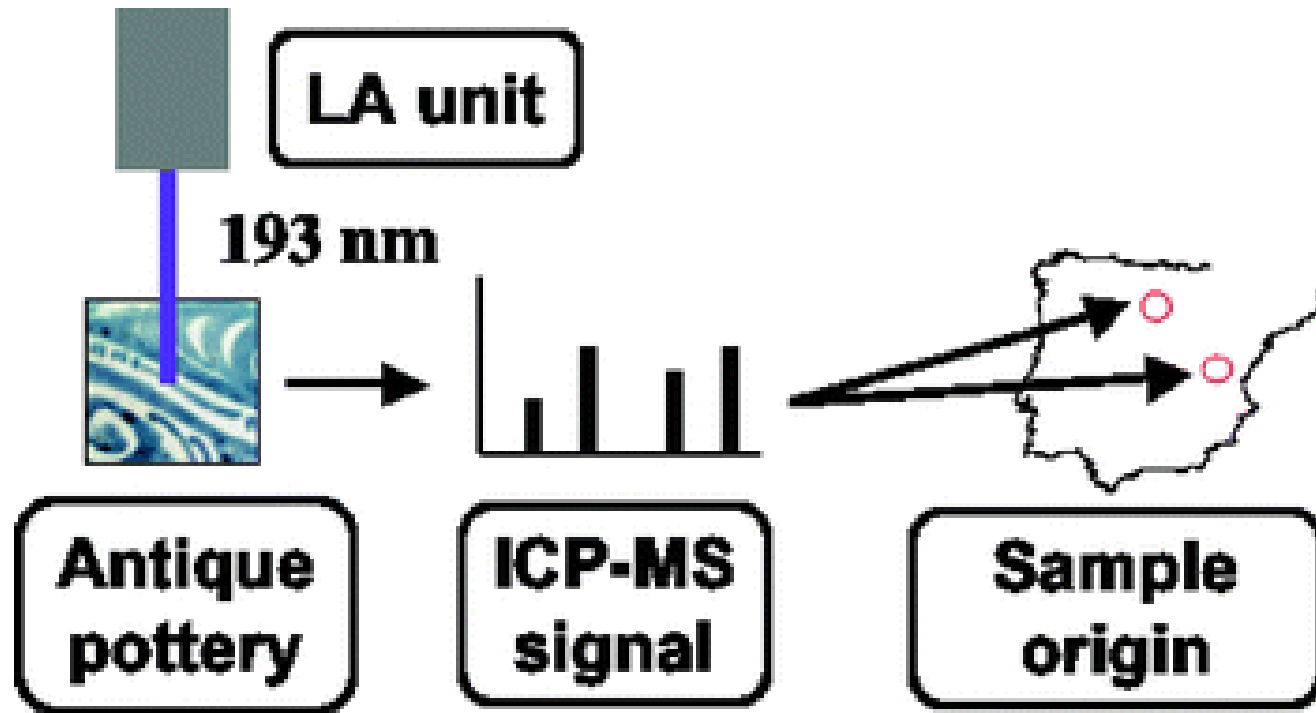
Kvadrupólový

TOF

Sektorový (MC)

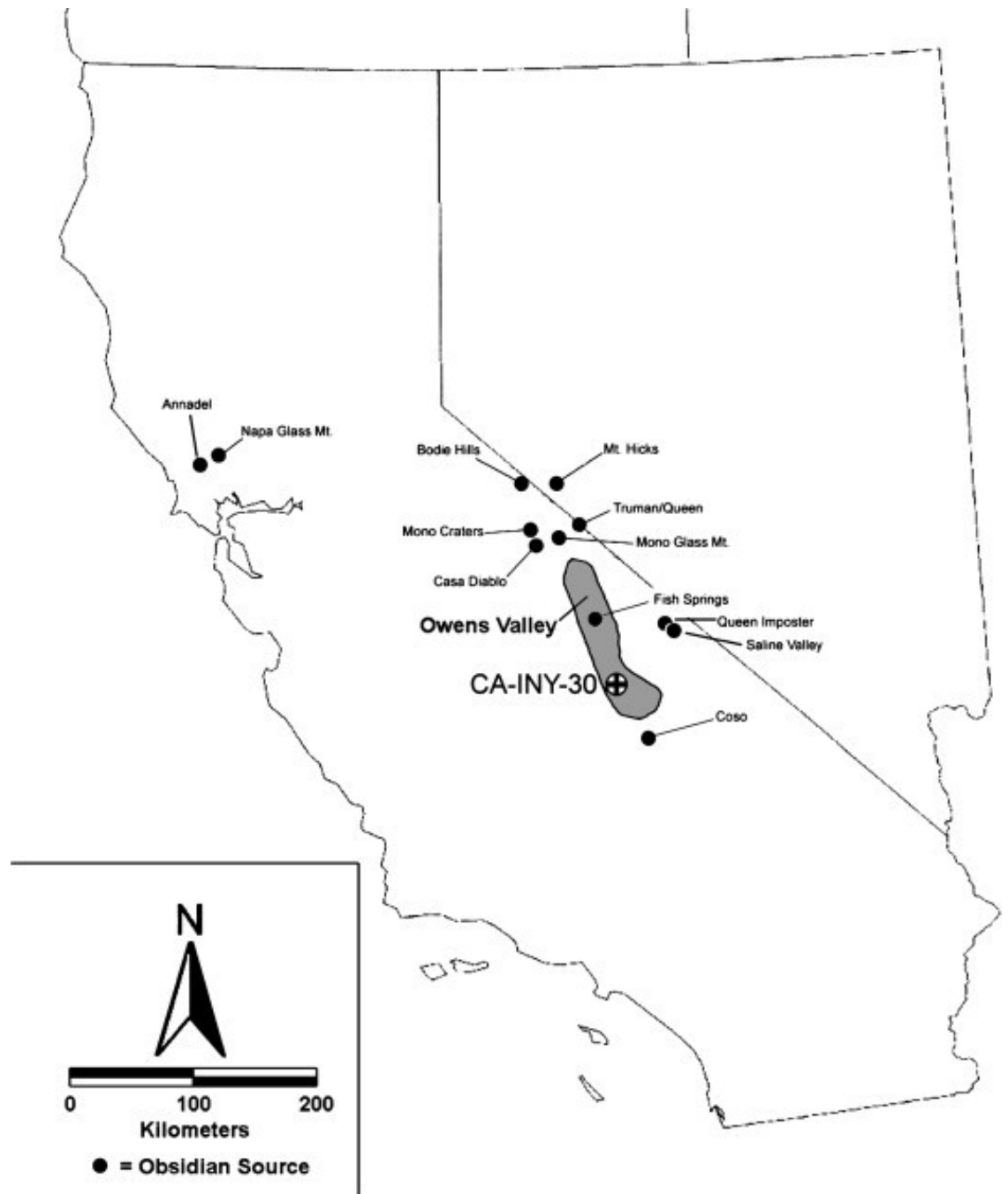


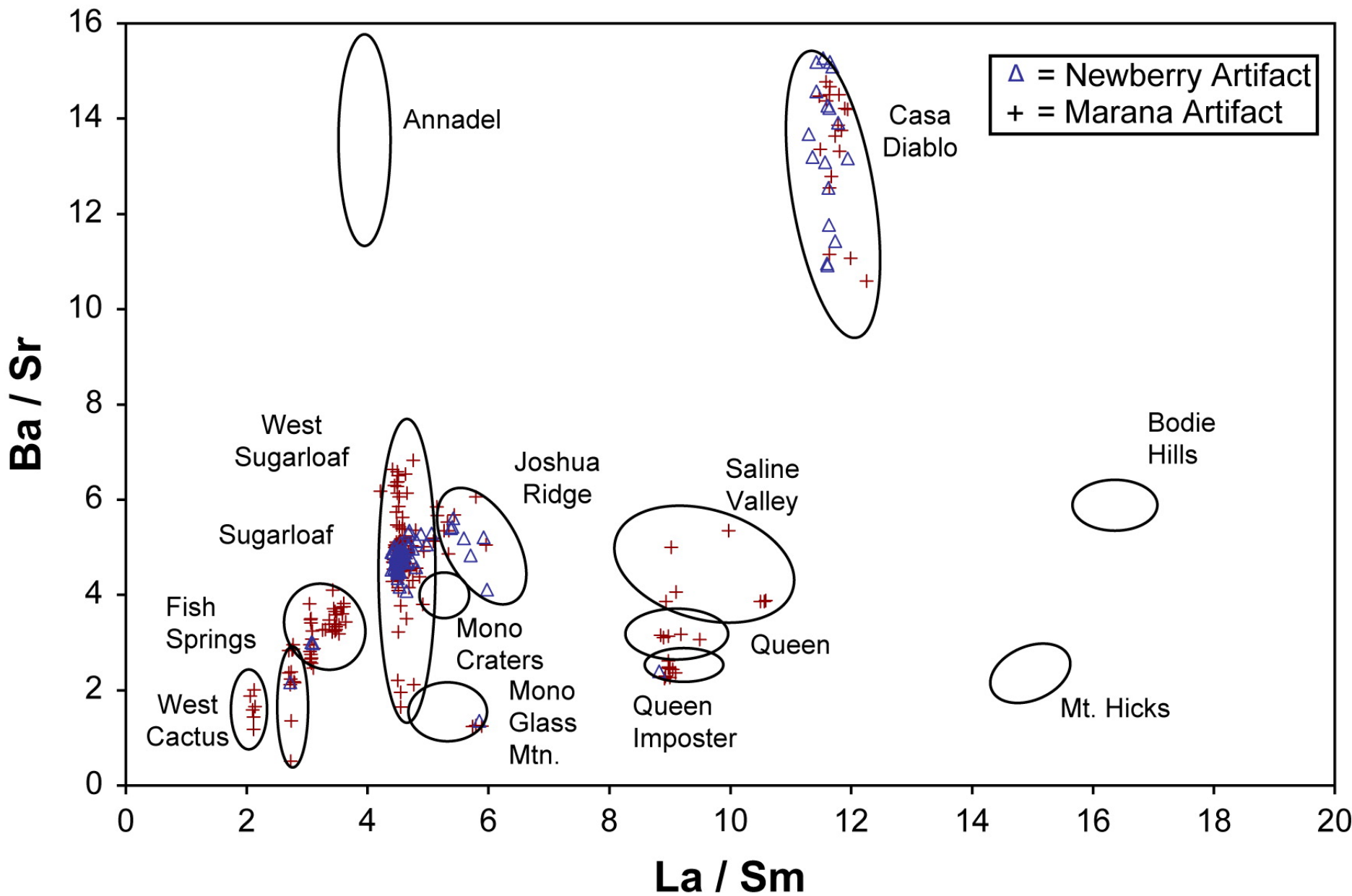
# Aplikace LA-ICP-MS



# Provenience obsidiánu

Owens Valley,  
vých. Kalifornie





# Malba na keramice

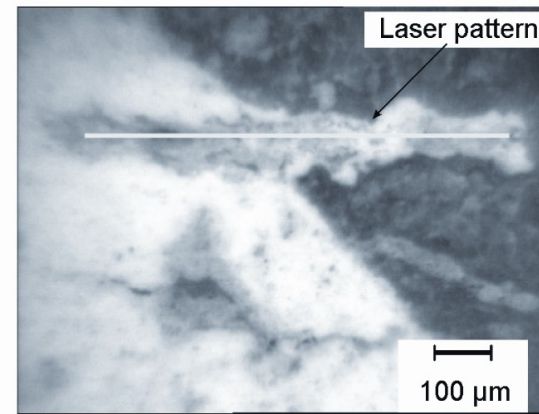


Fig. 5. Post-ablation photograph showing line pattern which has been ablated across the slip-decoration boundary of a Mimbres pottery sherd

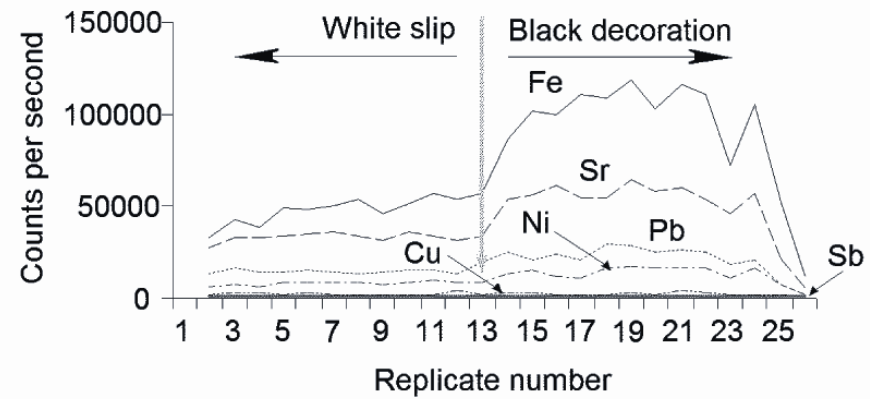
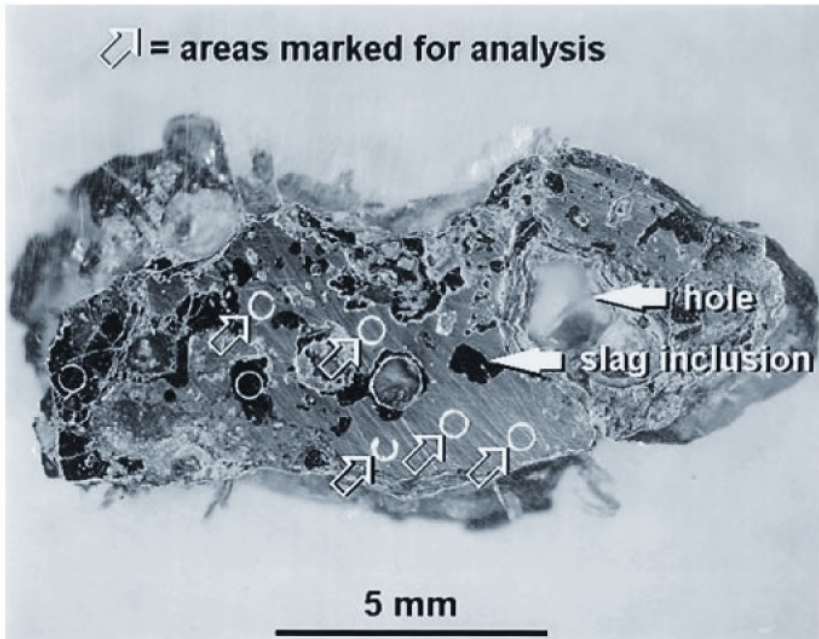


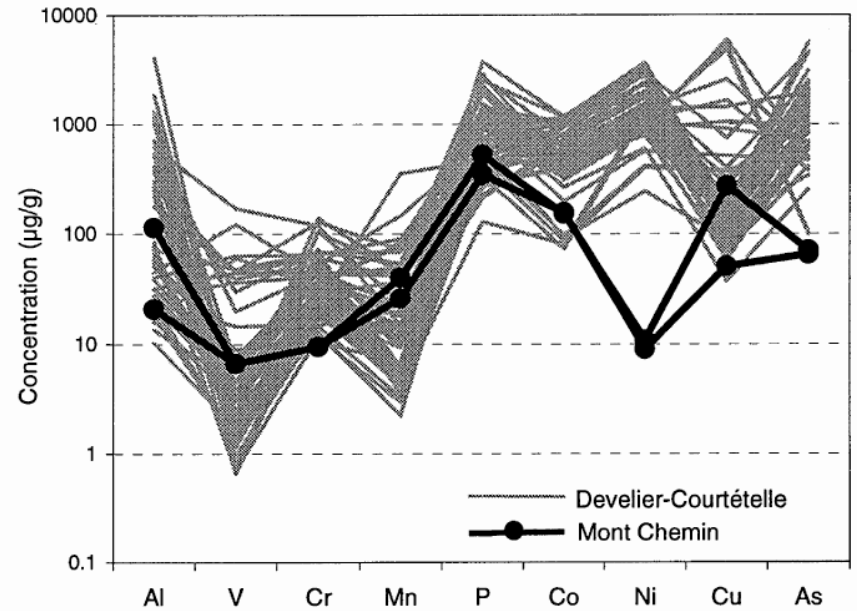
Fig. 6. Elemental scan showing replicate analyses over time as laser pattern is ablated across white slip to black decoration border on a Mimbres pottery sherd



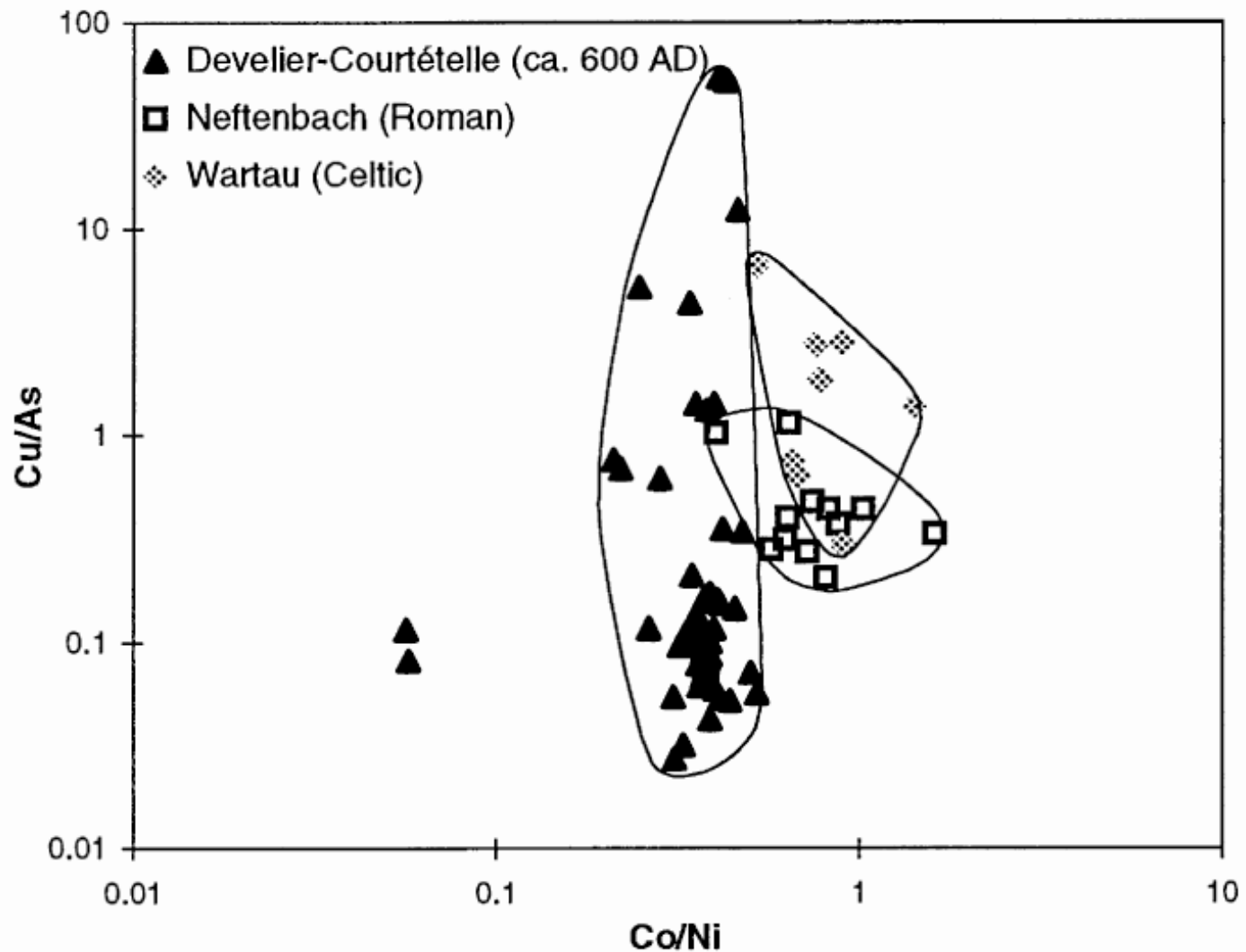
# Provenience železa



**Fig.1** Optical microscopy view of a cross-section of an iron bloom fragment embedded in a synthetic resin

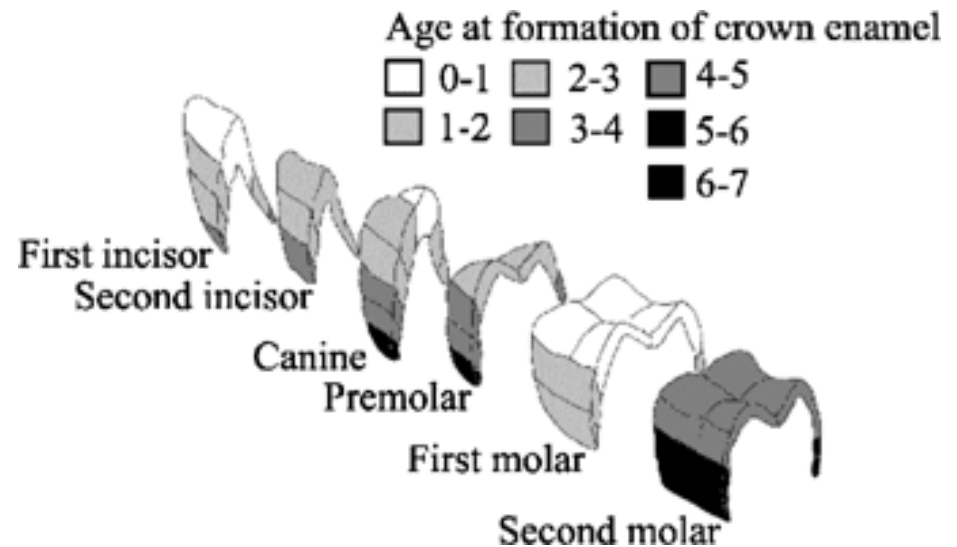
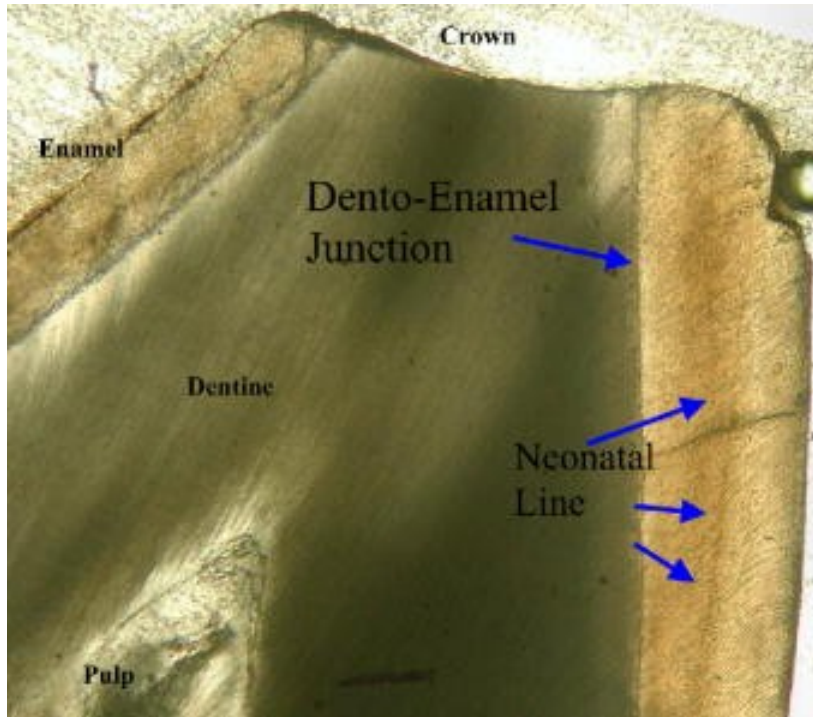
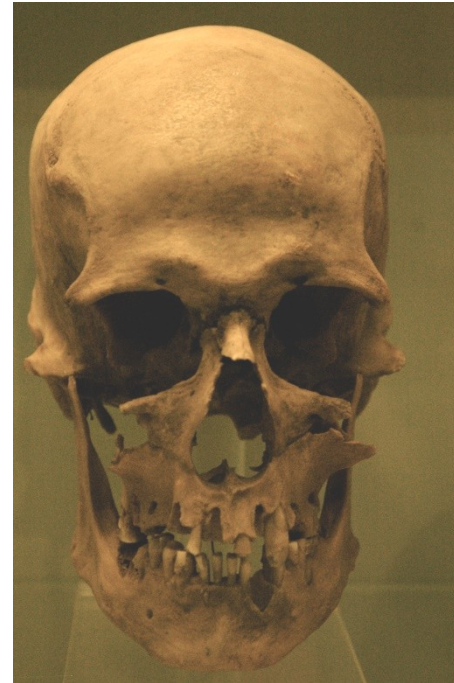


**Fig.9** Concentration profile for an iron bloom sample from Mont Chemin (Switzerland), compared to the concentration profiles in the Develier-Courtételle samples, showing low values for Ni in the Mont-Chemin sample



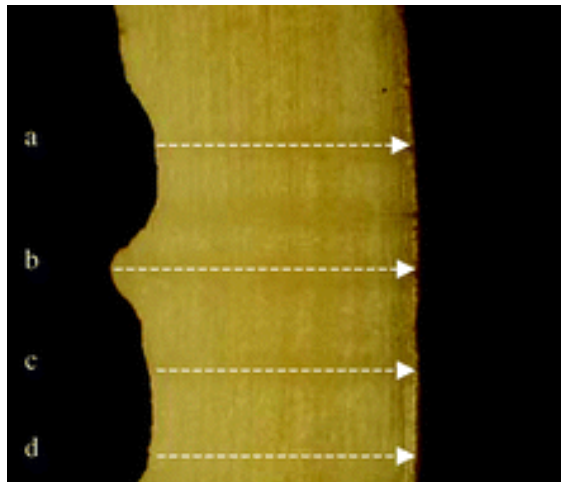
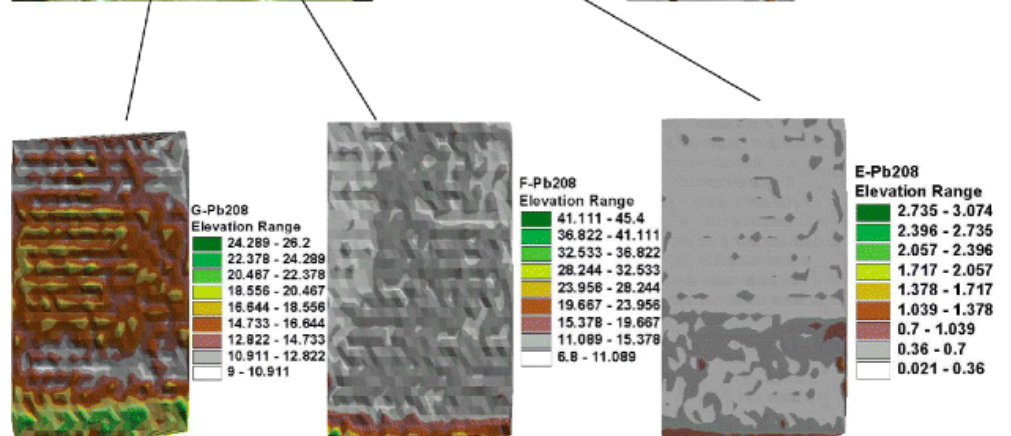
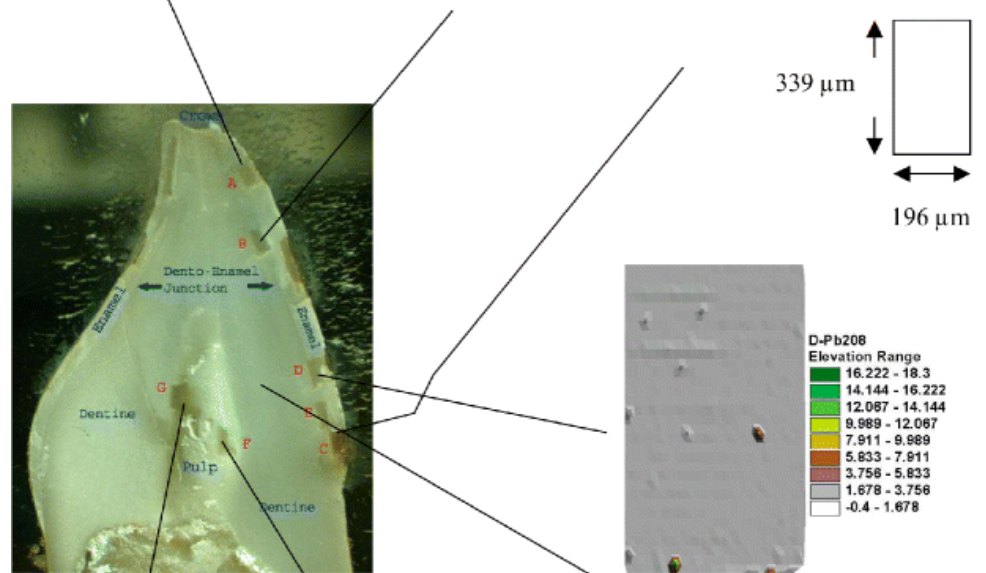
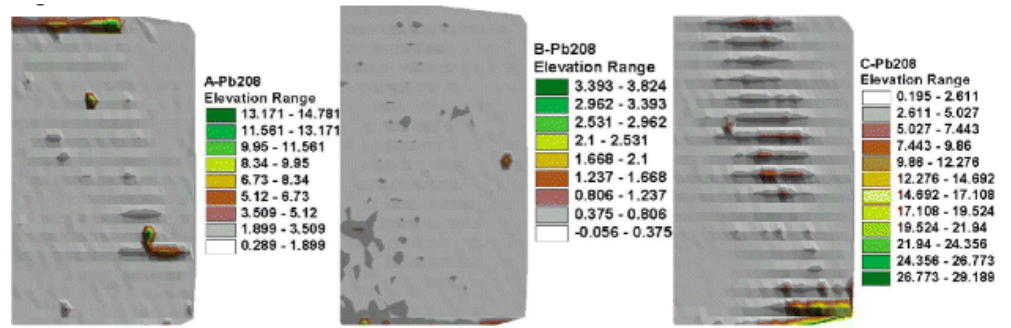
**Fig. 10** Plot of the Cu/As-ratio *versus* Co/Ni-ratio in archaeological iron samples from Neftenbach (Roman), Wartau (Celtic) and Develier-Courtételle (early medieval), measured by LA-ICP-MS

# Analýza zubní skloviny

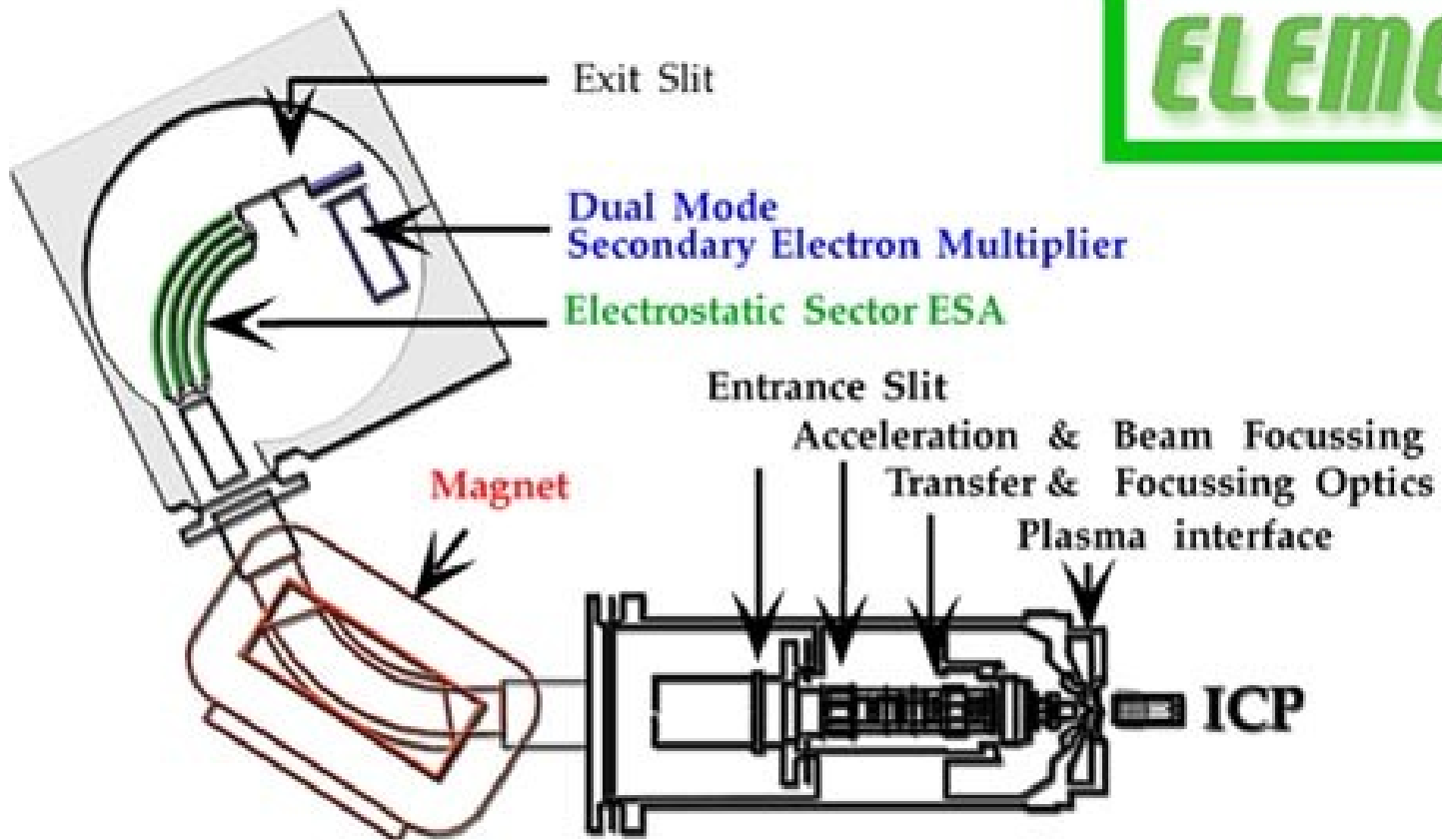


Liniové skeny

Plošné skeny

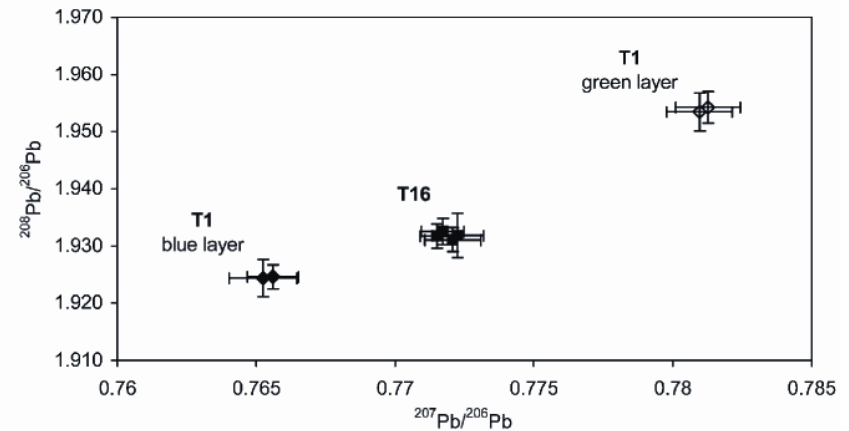


# MC LA-ICP-MS

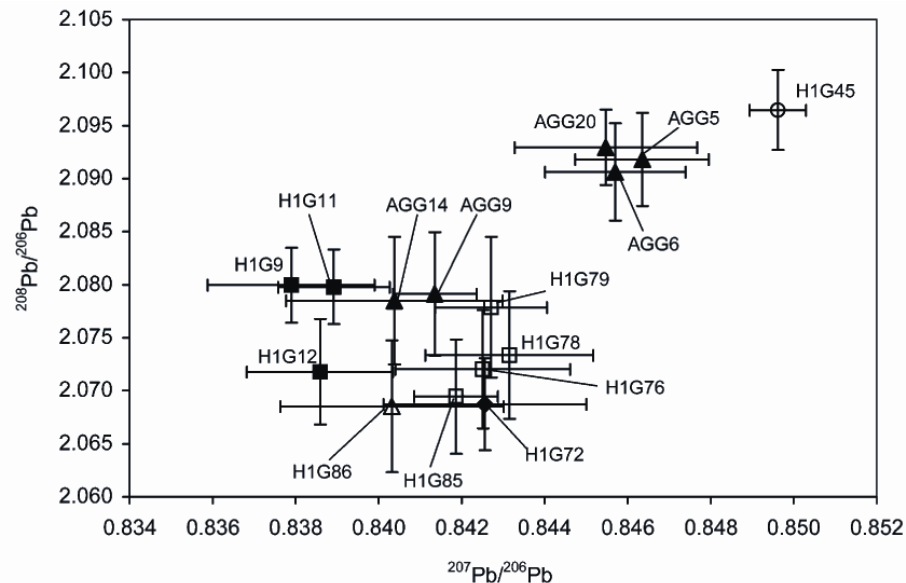


# Analýza izotopových poměrů

## Sklo „Art nouveau“



**Fig. 2** Lead isotope ratio distribution of the two iridescent Art Nouveau glasses. Glass T1 consists of two layers of approximately equal thickness (coloured green and blue, respectively). Error bars represent total combined uncertainties ( $k = 1$ ).



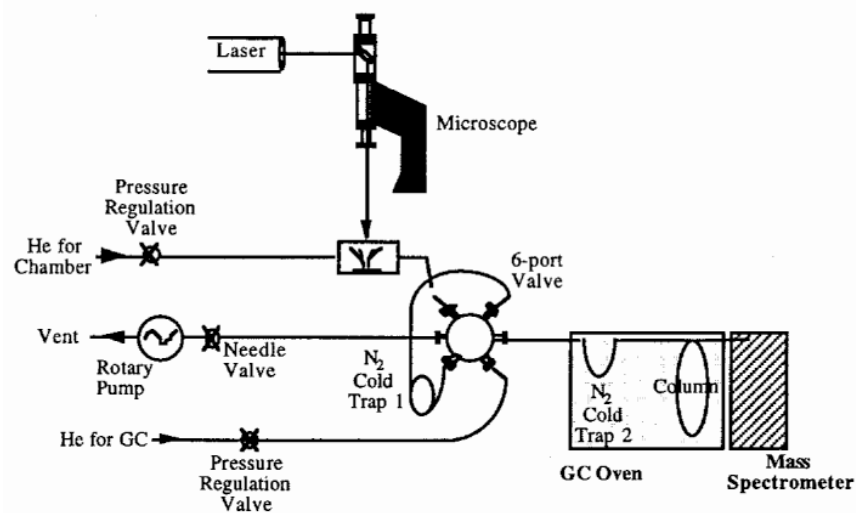
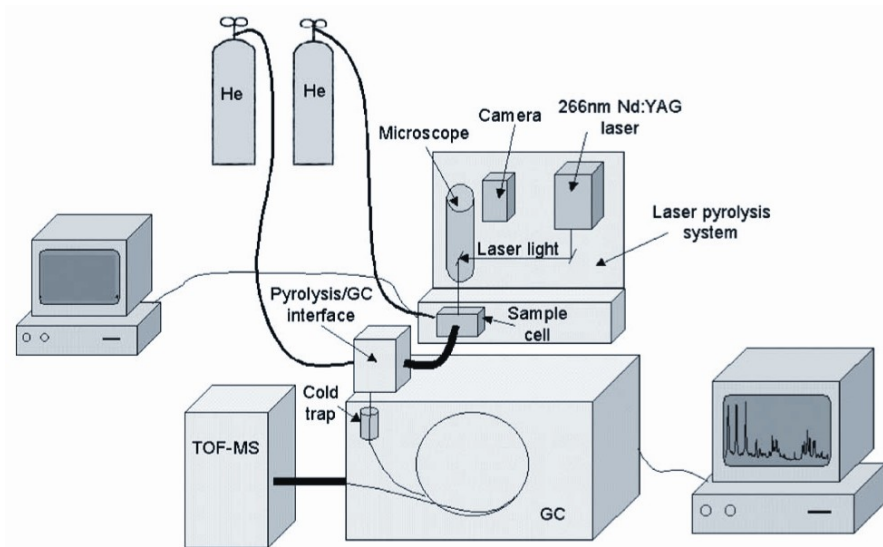
**Fig. 3** Lead isotope ratios of Ephesos glass samples after external mass bias correction *via* the NIST SRM 610 glass reference material. Error bars represent total combined uncertainties ( $k = 1$ ). For sample description see Table 1.

# Ostatní aplikace

- Kovové předměty (provenience, technologie)
- Rukopisy a malby (pigmenty)
- Keramika a porcelán
- Drahé kameny (provenience, napodobeniny)

# Laserová mikropyrolýza

Nd:YAG 1064 nm



Spojení s GC-MS



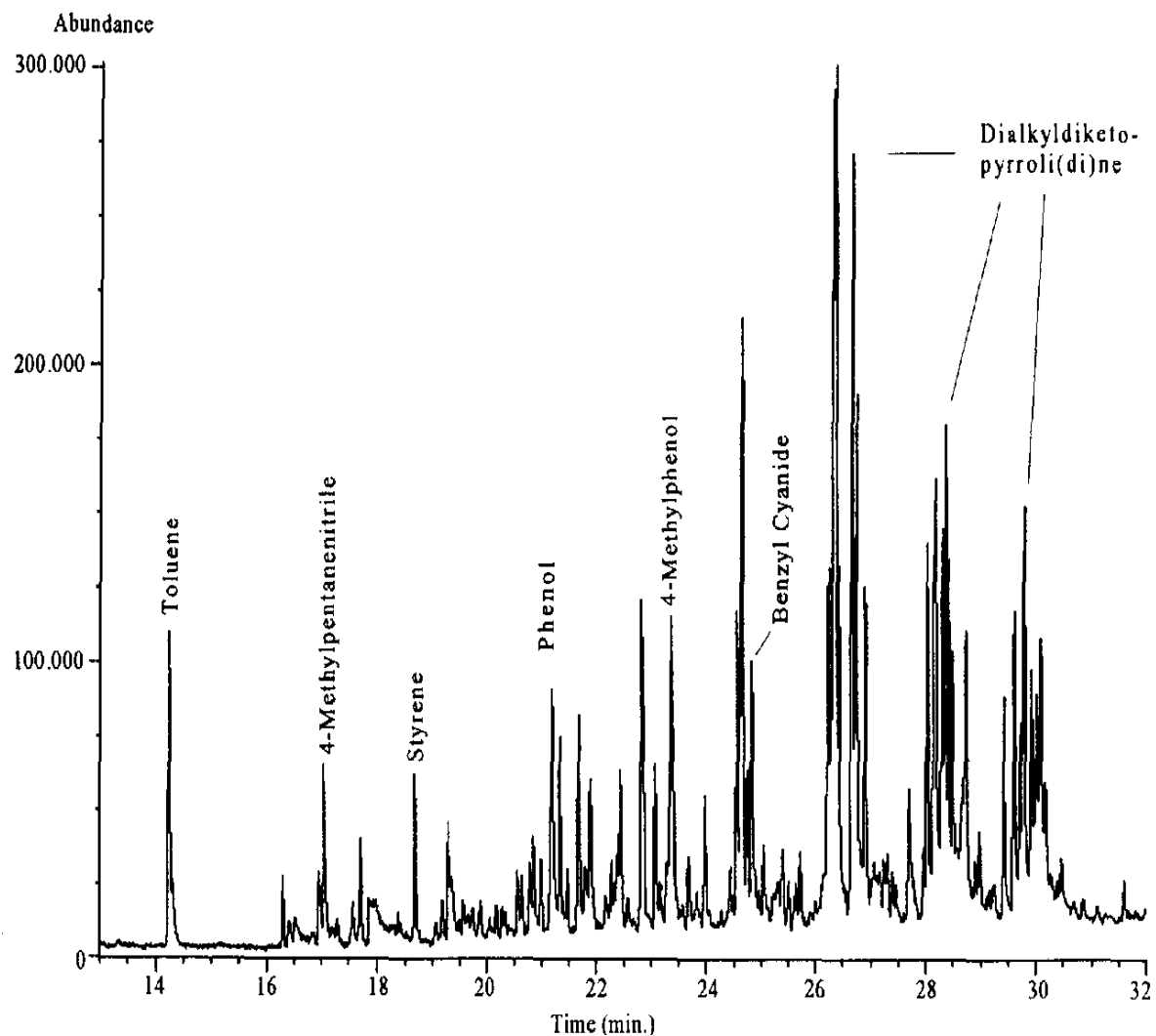
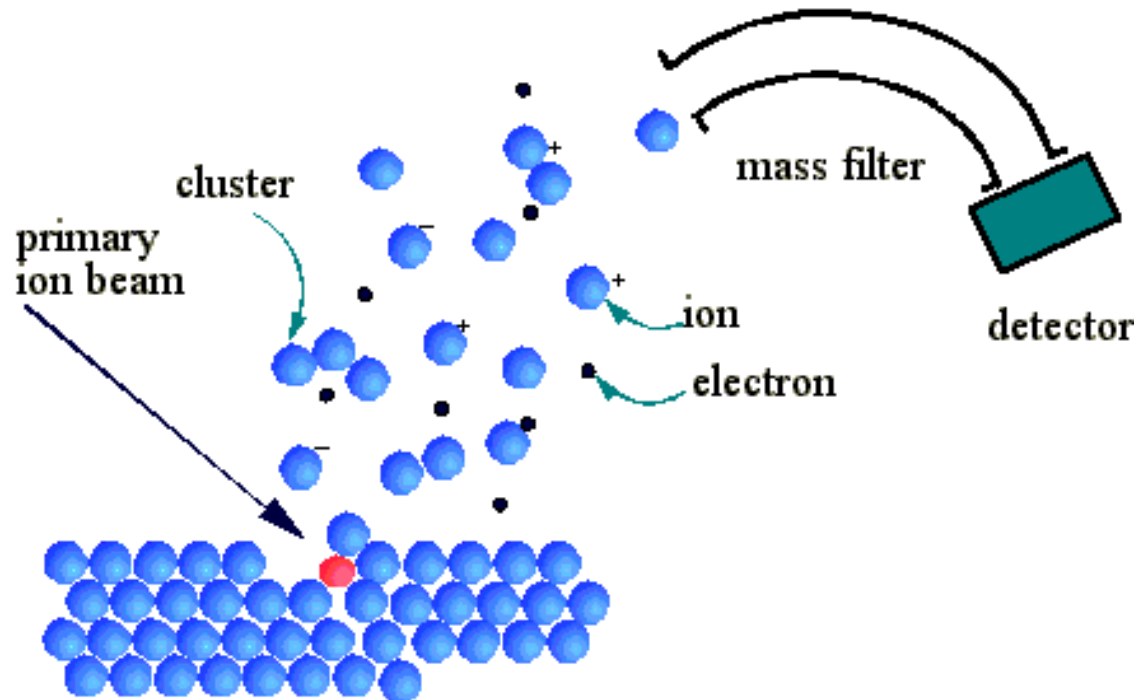


Fig. 1. Laser pyrolysis GC-MS chromatogram of volatile organics from native pig muscle, irradiated with a CO<sub>2</sub>-laser (10 W, 1 kW cm<sup>-2</sup>, aerosol sampled on carbotrap adsorber, desorption with carbon disulfide, on-column injection).

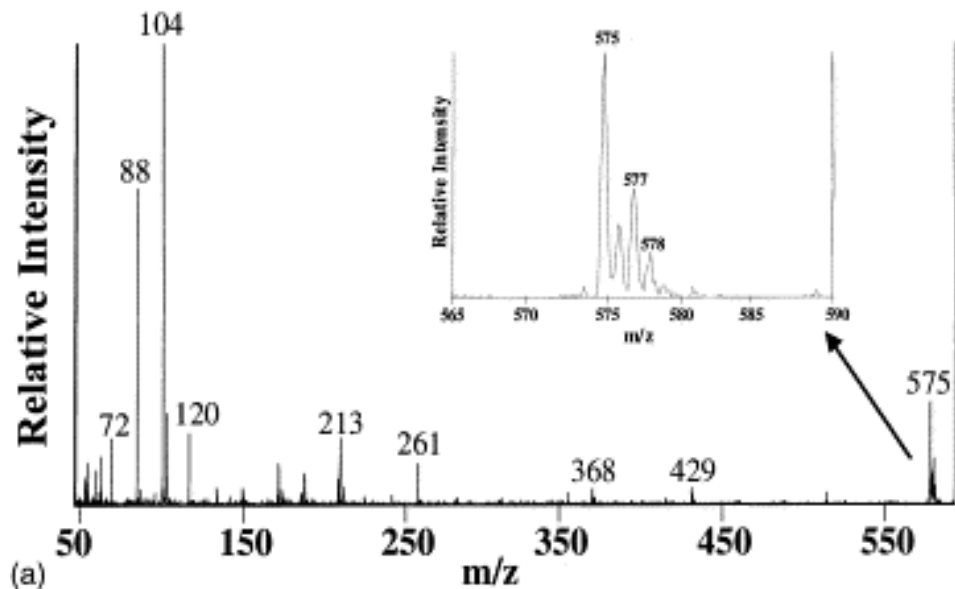
# LDI - TOF

Desorpce a ionizace laserem



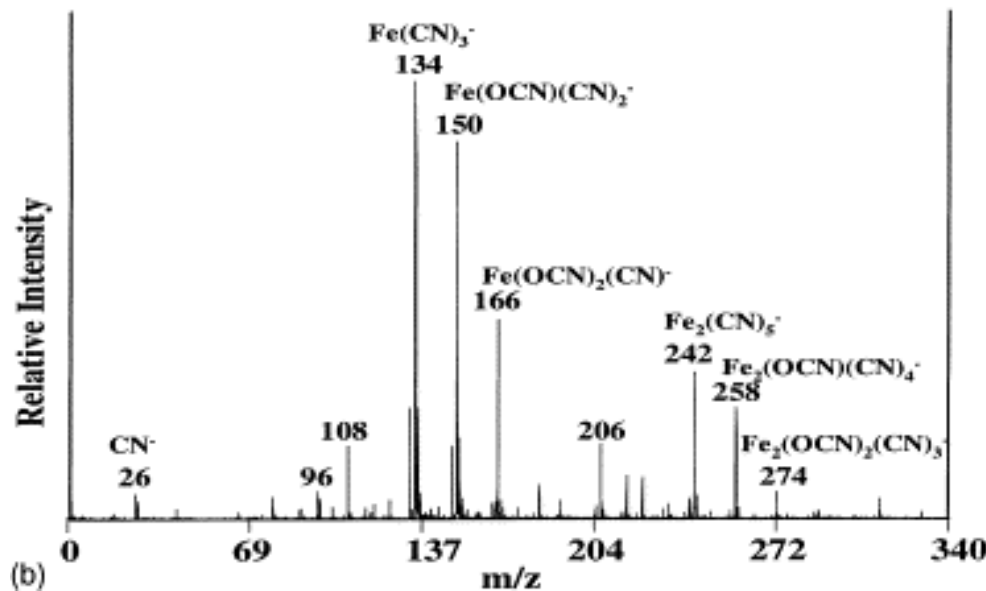
# Analýza pigmentů

Pruská modř



(a)

$m/z$	Assignment	Fe oxidation states
108	$\text{Fe}(\text{CN})_2^-$	+1
124	$\text{Fe}(\text{OCN})(\text{CN})^-$	+1
134	$\text{Fe}(\text{CN})_3^-$	+2
150	$\text{Fe}(\text{OCN})(\text{CN})_2^-$	+2
166	$\text{Fe}(\text{OCN})_2(\text{CN})^-$	+2
182	$\text{Fe}(\text{OCN})_3^-$	+2
190	$\text{Fe}_2(\text{CN})_3^-$	(+1, +1) or (0, +2)
206	$\text{Fe}_2(\text{OCN})(\text{CN})_2^-$	(+1, +1) or (0, +2)
216	$\text{Fe}_2(\text{CN})_4^-$	(+1, +2) or (0, +3)
222	$\text{Fe}_2(\text{OCN})_2(\text{CN})^-$	(+1, +1) or (0, +2)
242	$\text{Fe}_2(\text{CN})_5^-$	(+2, +2) or (+1, +3)
258	$\text{Fe}_2(\text{OCN})(\text{CN})_4^-$	(+2, +2) or (+1, +3)
274	$\text{Fe}_2(\text{OCN})_2(\text{CN})_3^-$	(+2, +2) or (+1, +3)



(b)

# Pigmenty v iluminovaných rukopisech

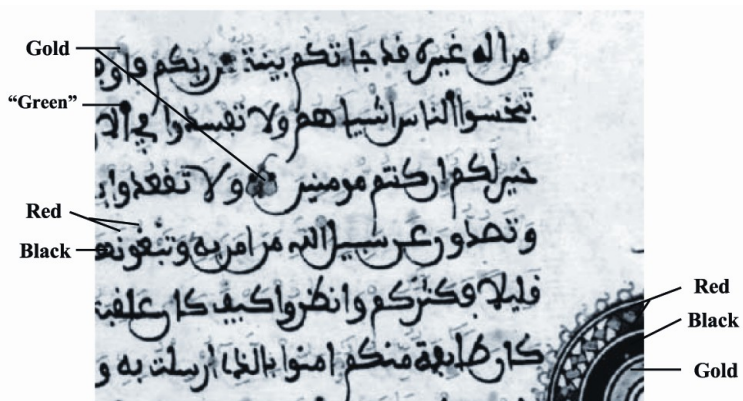


Figure 4 A portion of the page of the Qur'an used in this study.

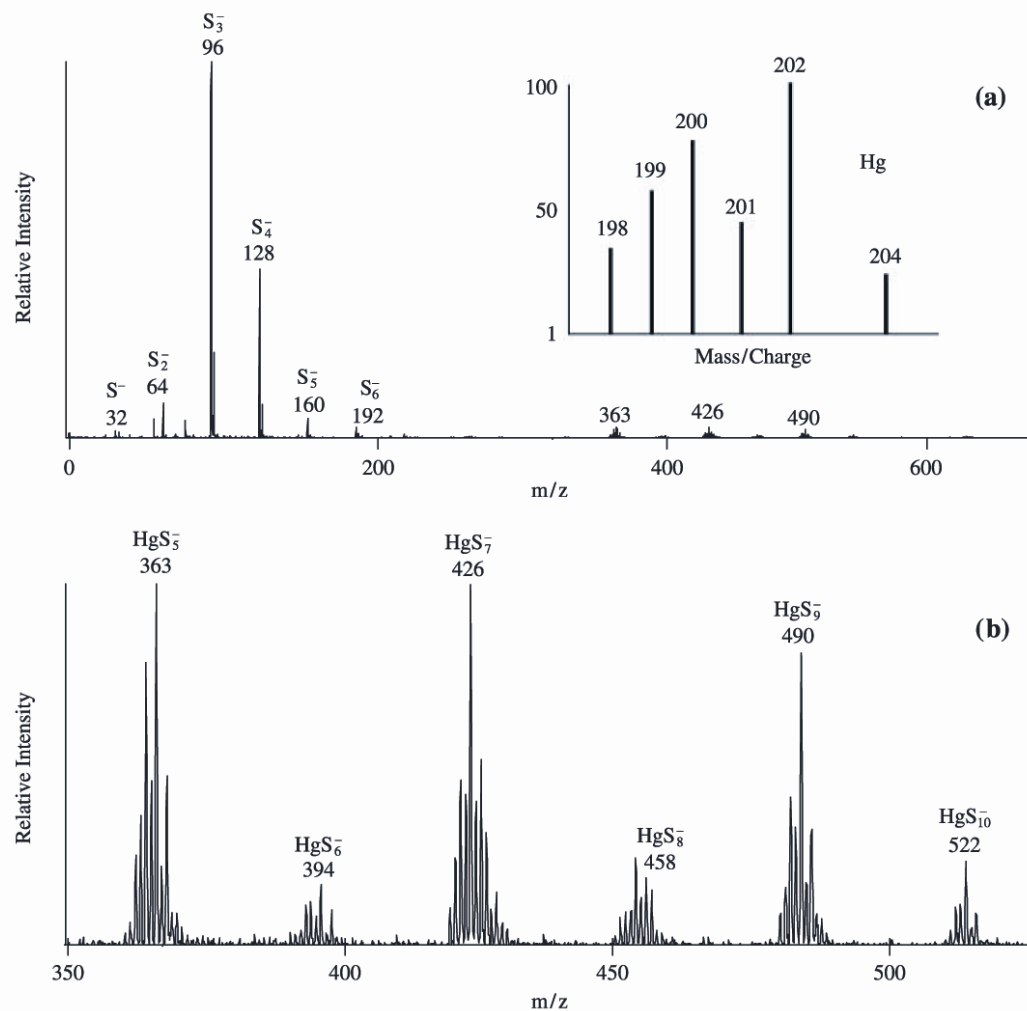


Figure 5 (a) A negative ion LDMS spectrum of the red ink/dye region of the Qur'an sample. (b) An expanded view of the higher  $m/z$  portion of the spectrum.



# Akrylátové barvy

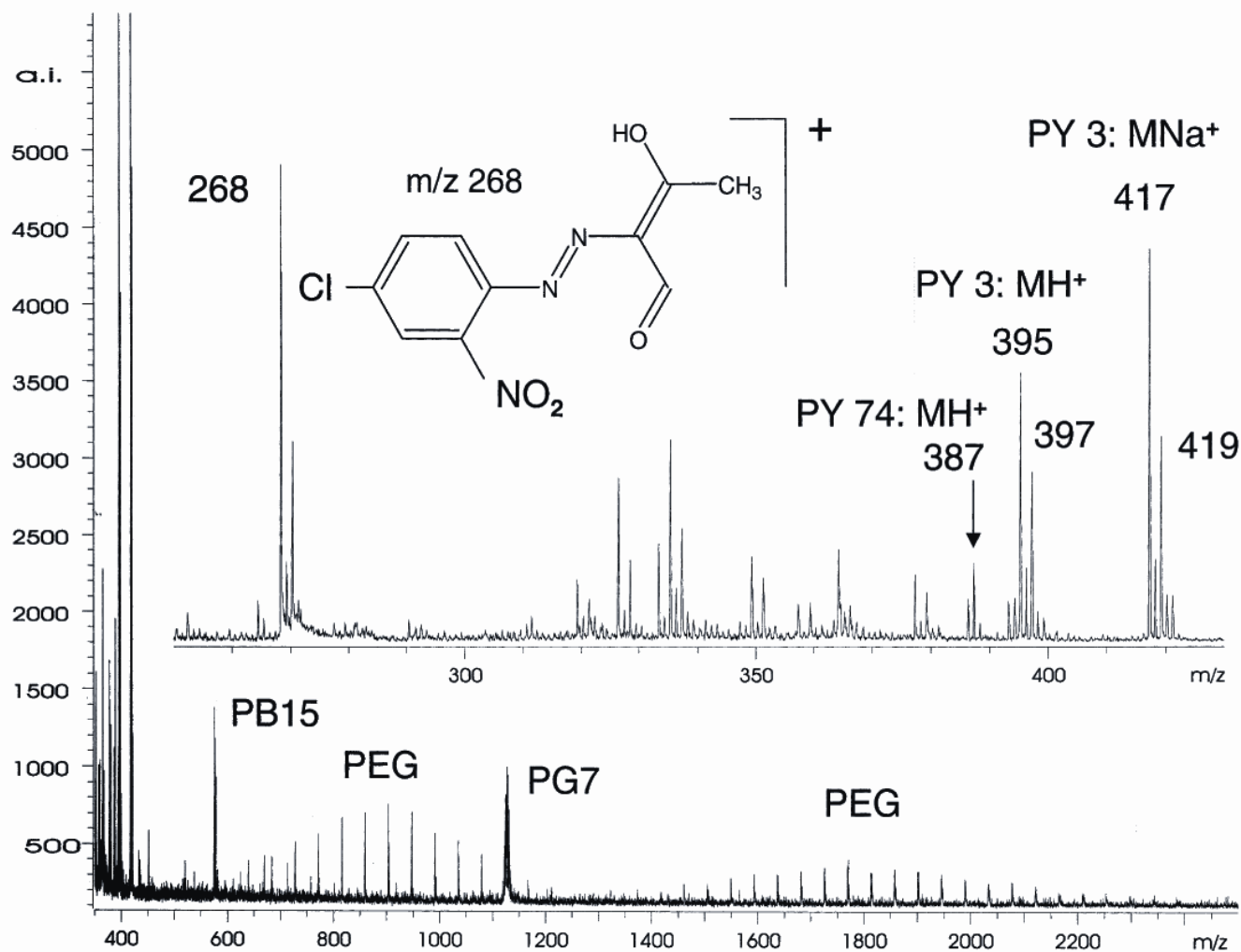
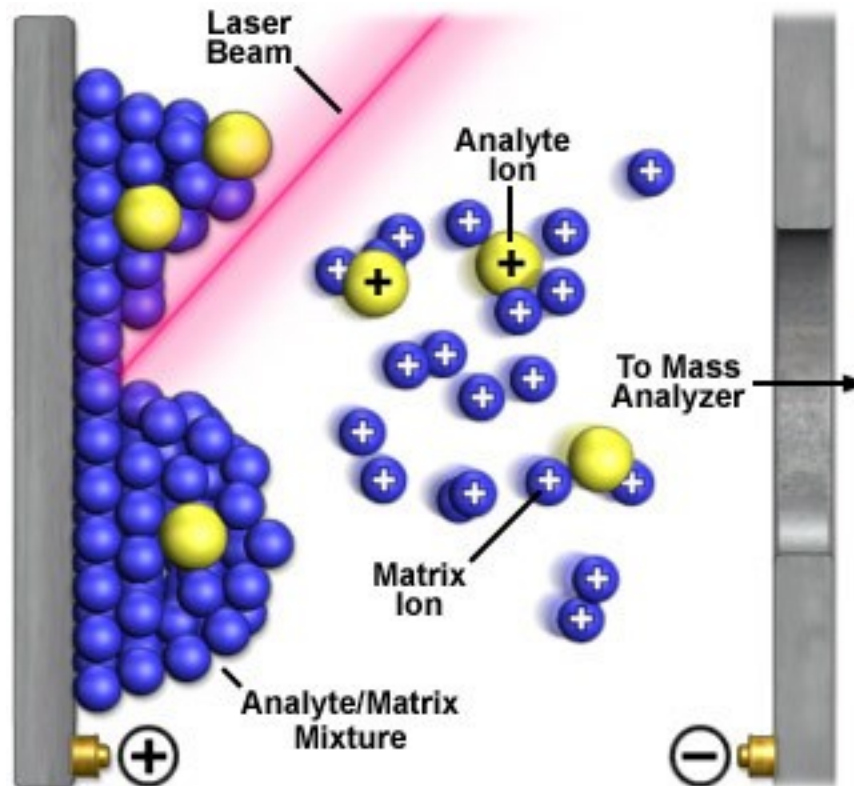


Fig. 11. Laser desorption ionisation mass spectrum of Winsor and Newton Finity 'Permanent Green Light' acrylic paint. The paint was painted on cellulose TLC plate surface and after drying analysed directly by LDI-TOFMS using a nitrogen laser at 337 nm.

# MALDI-TOF

Desorpce a ionizace laserem za přítomnosti matrice

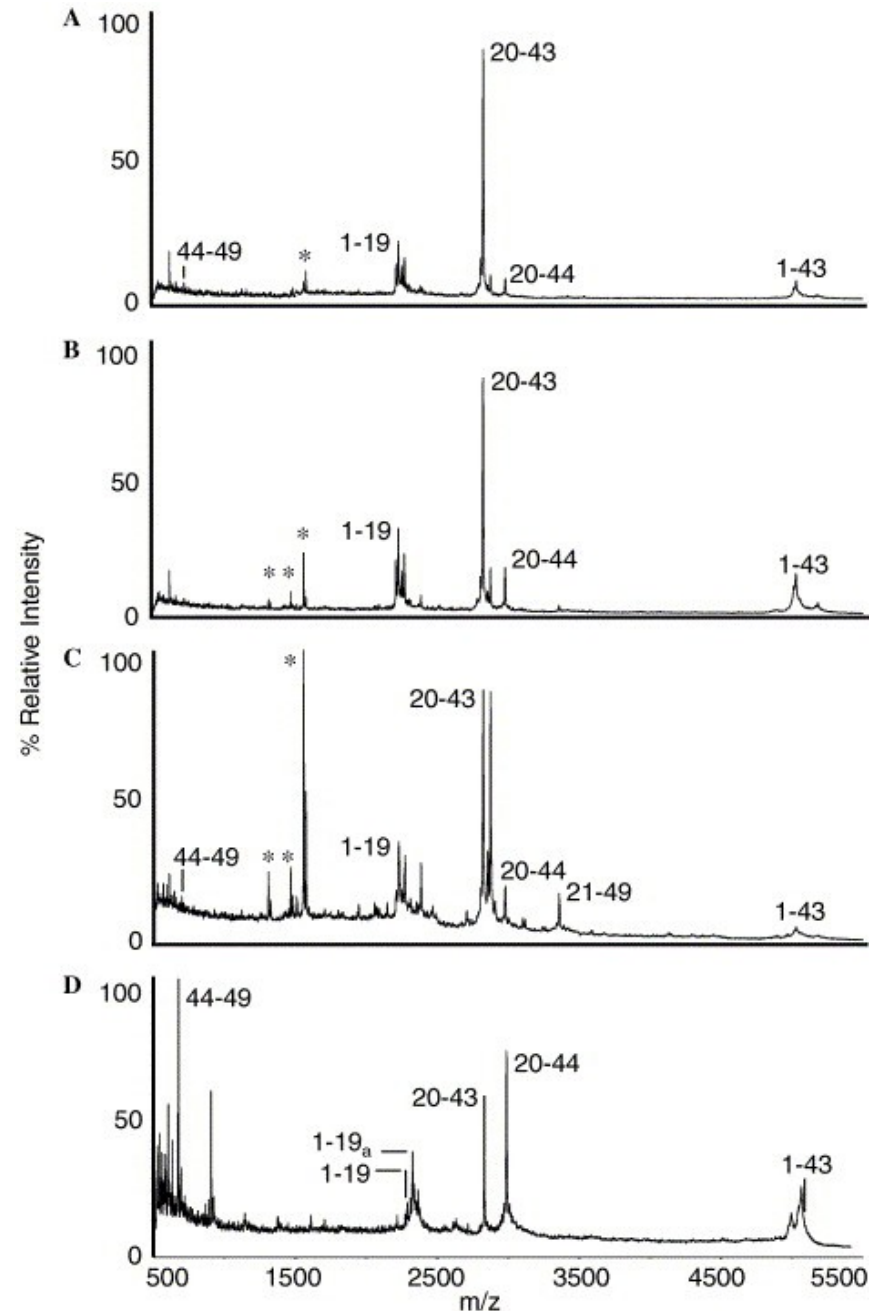


# Analýza fosilních proteinů



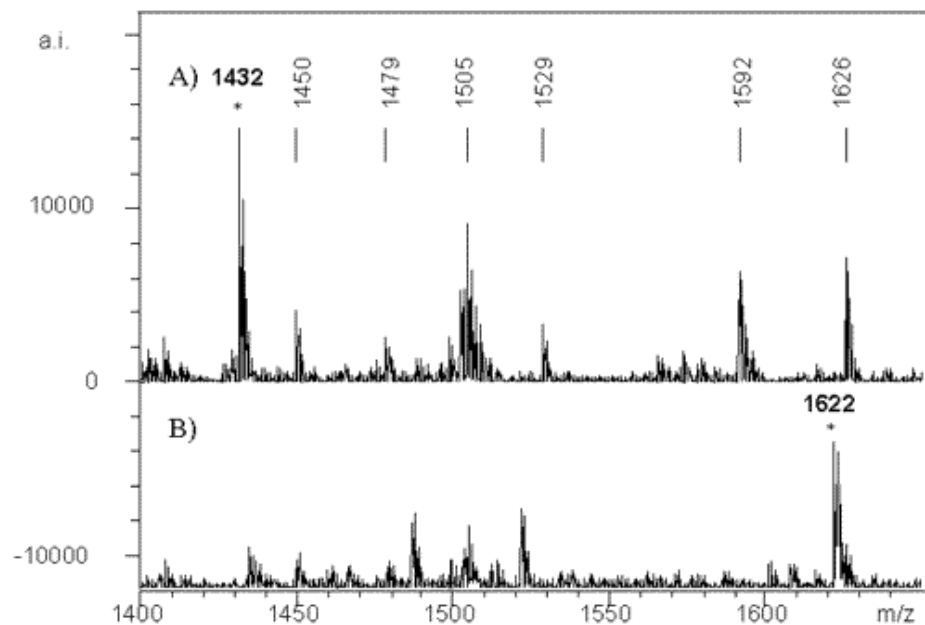
„Peptide mass fingerprint“ osteokalcinu rozloženého trypsinem:

- (A) extant horse
- (B) zebra
- (C) osel
- (D) částečně čištěný osteokalcin z 42 000 let starých pozůstatků koně.

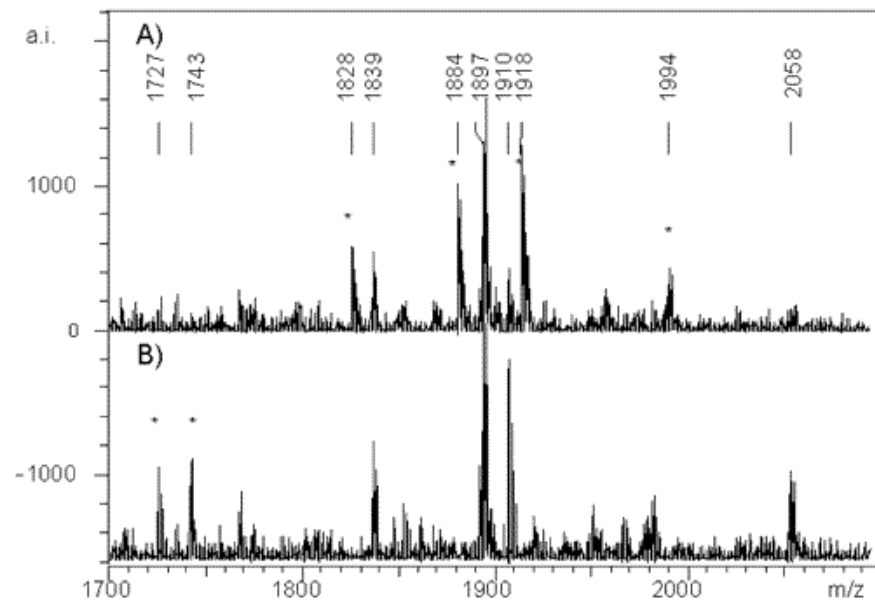


# Identifikace keratinů

Hmotnostní spektra 1400 to 1700 Da vlny jaka (A) a kašmírské kozy (B) (rozklad trypsinem).



Hmotnostní spektra 1700 to 2100 Da peří husy (A) a kachny (B).

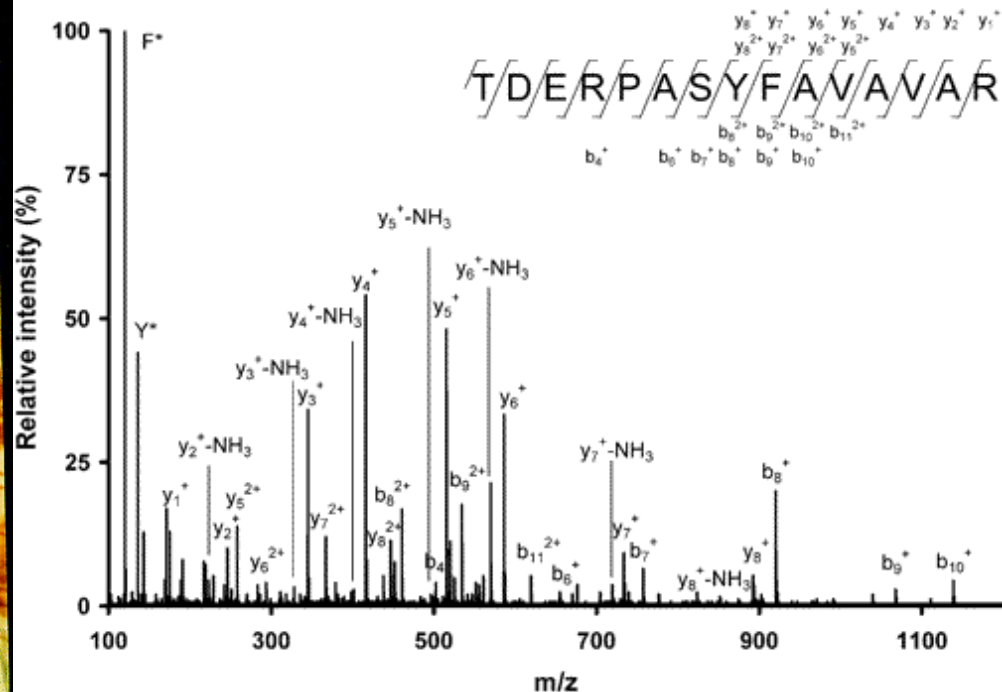




# Identifikace organických poživ v malbách

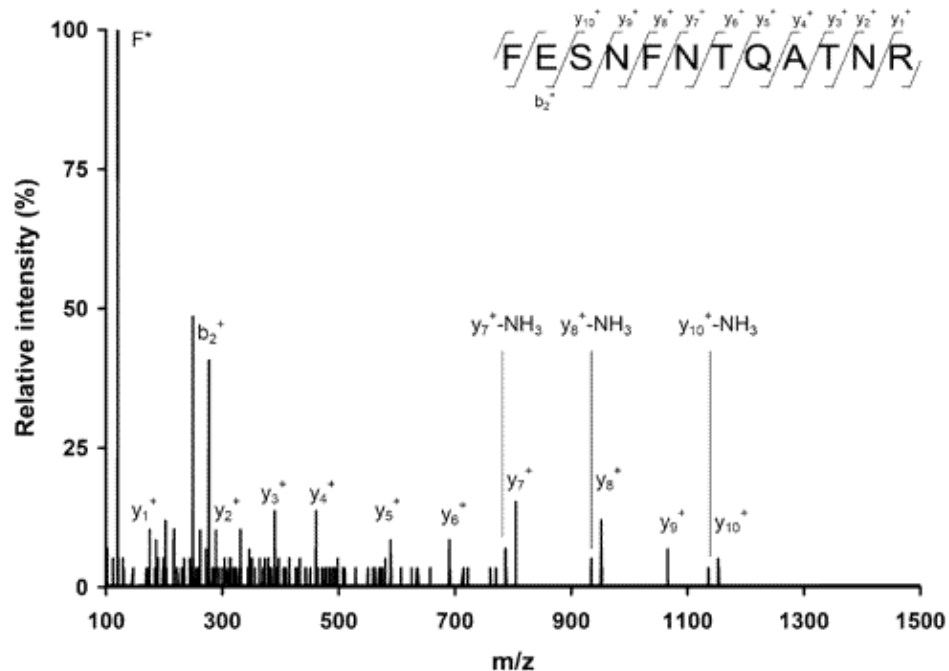


Triptych Benedetta Bonfigliho, Madona s dítětem, sv. Jan Křtitel. sv. Šebestián (XV. století).



MS/MS spektrum trojnásobně nabitých iontů pro  $m/z$  551.61, z hydrolyzovaného extraktu. Přítomny jsou y a b fragmenty peptidu ovotransferrinu 443-457 (TDERPASYFAVAVAR).

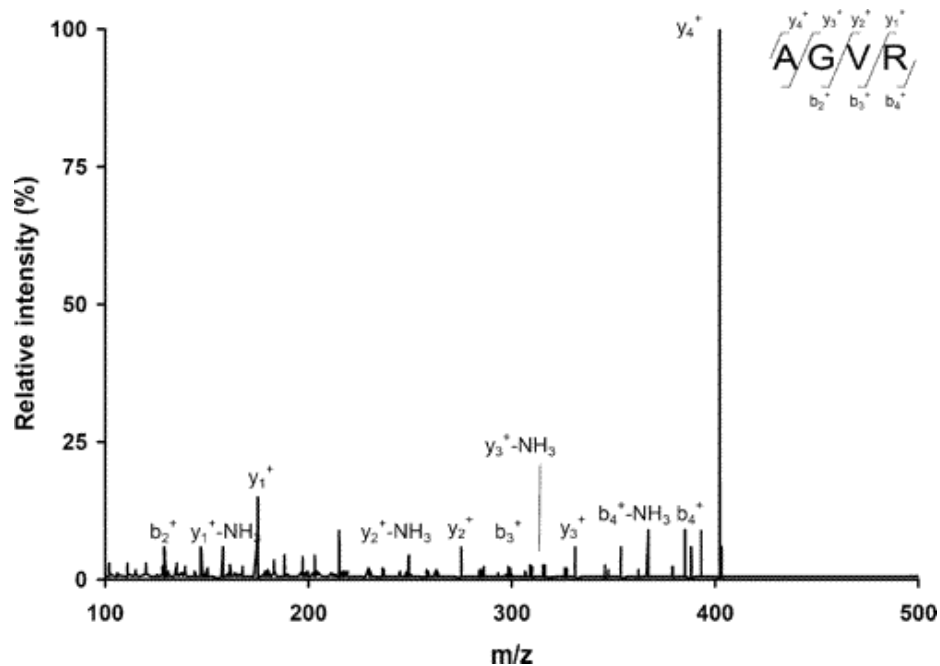
MS/MS spektrum dvojnásobně nabitých iontů  $m/z$  714.82, z hydrolyzovaného extraktu z triptychu Benedetta Bonfigliho. Přítomny jsou fragmenty **y** and **b** fragmentu peptidu lysozymu 52-63 (FESNFNTQATNR).



Závěr:

jako pojivo byly v triptychu Benedetta Bonfigliho použity vaječný bílek a žloutek triptych.

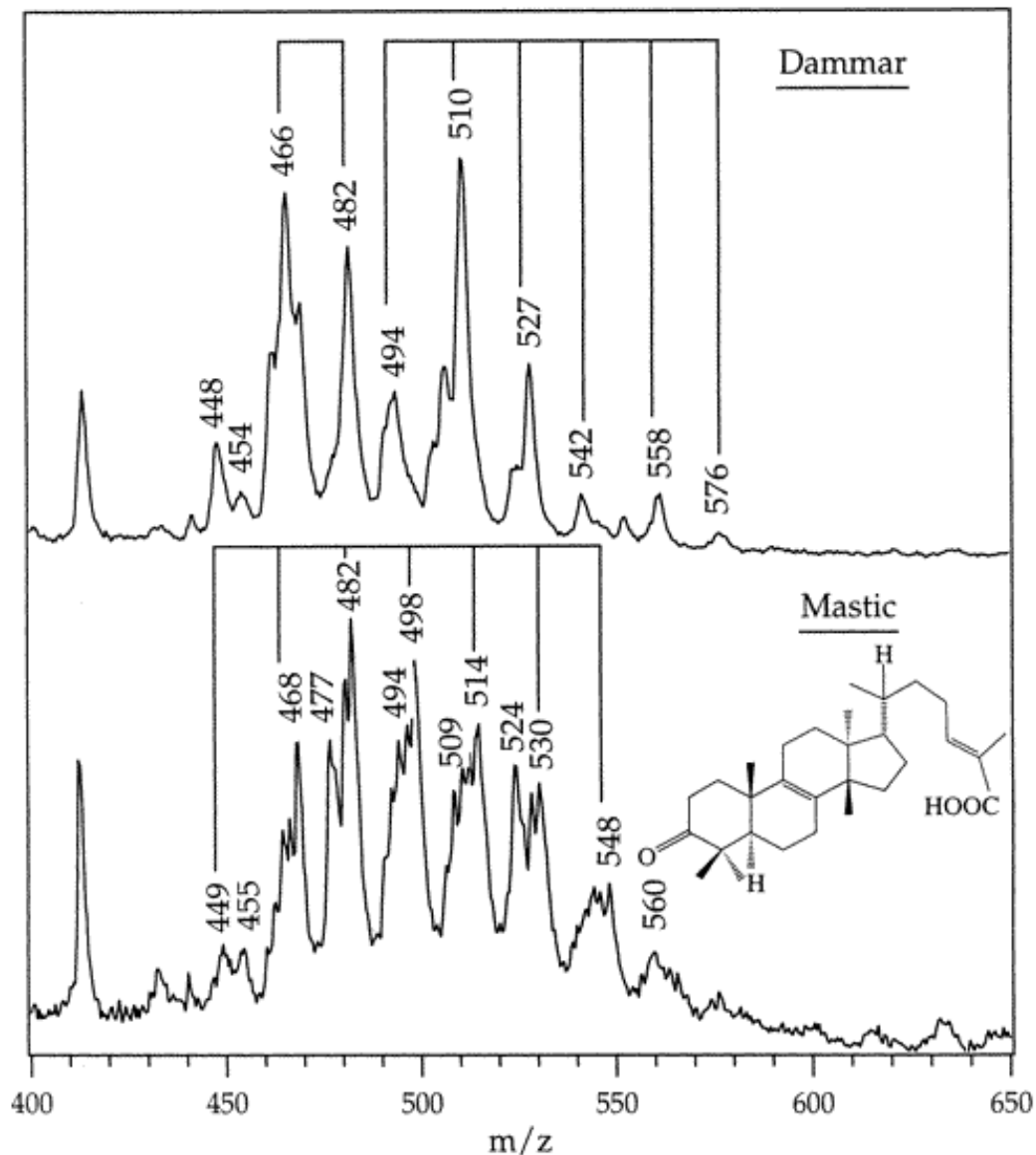
MS/MS spektrum  $m/z$  402.28, z hydrolyzovaného extraktu z triptychu Benedetta Bonfigliho. Přítomny **y** a **b** fragmenty peptidu vitellogeninu II 50-53 (AGVR).



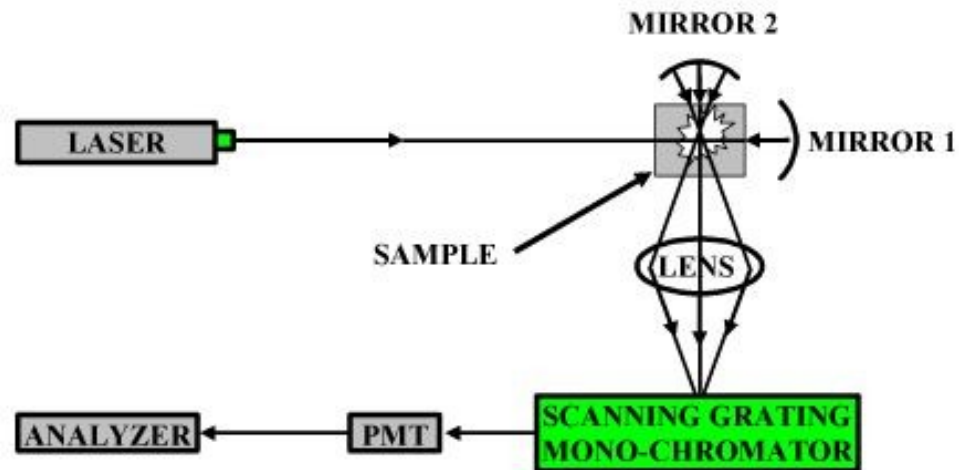
# Degradace historických laků

Fotochemická degradace přírodních triterpenoidů použitých jako laky

Hmotnostní spektra laserové desorpce/ionizace dammaru (nahore) a mastixu (dole) na grafitu.

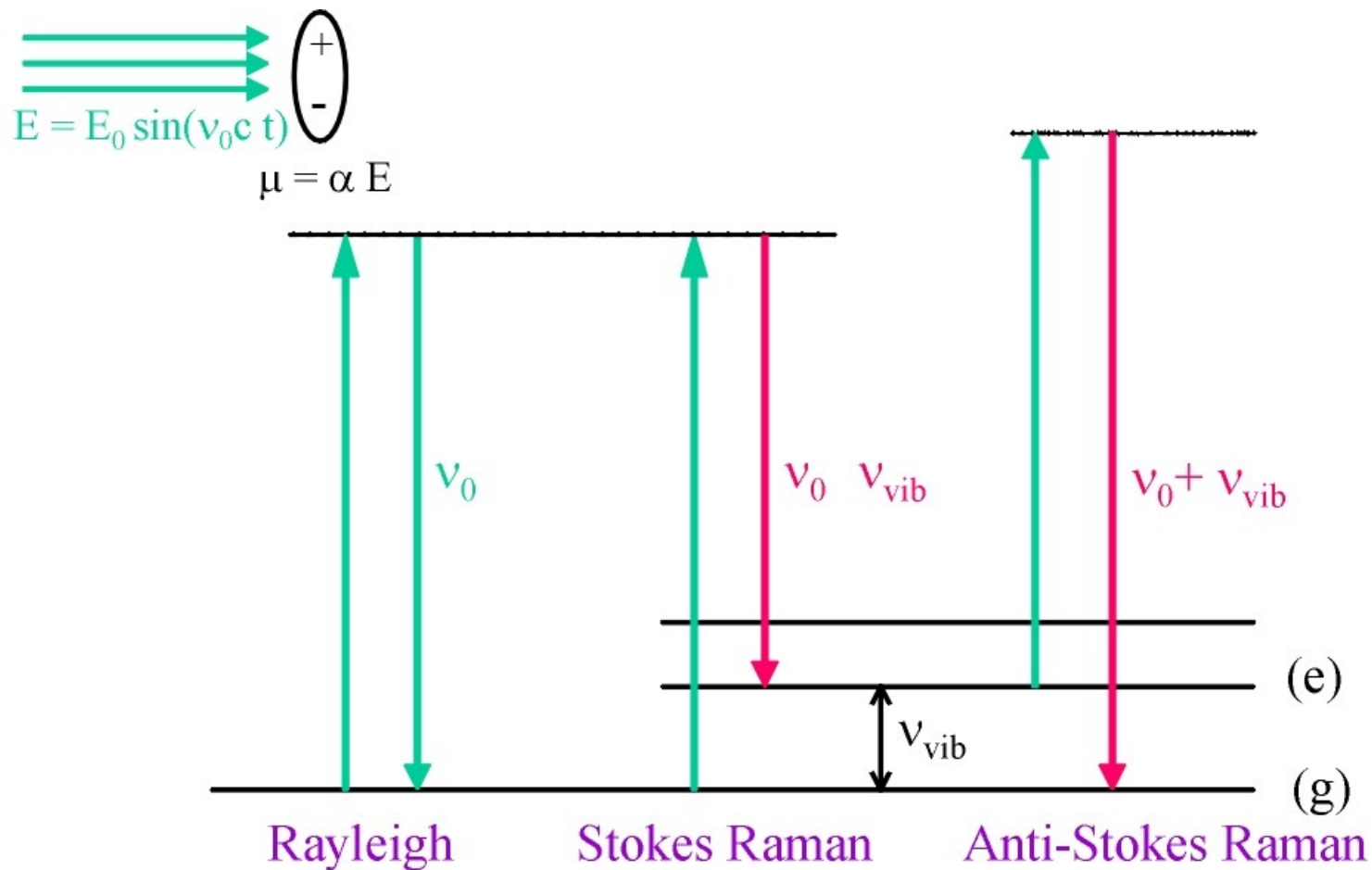


# Ramanova spektrometrie



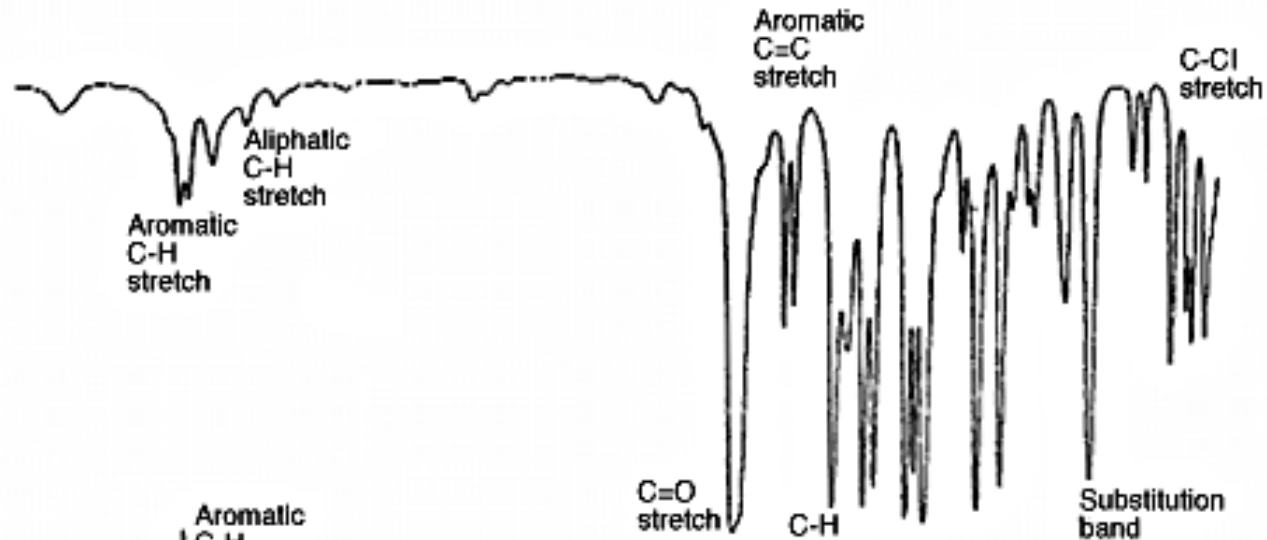
Nd:YAG	1064 nm
He-Ne	632.8 nm

# Princip Ramanovy spektrometrie

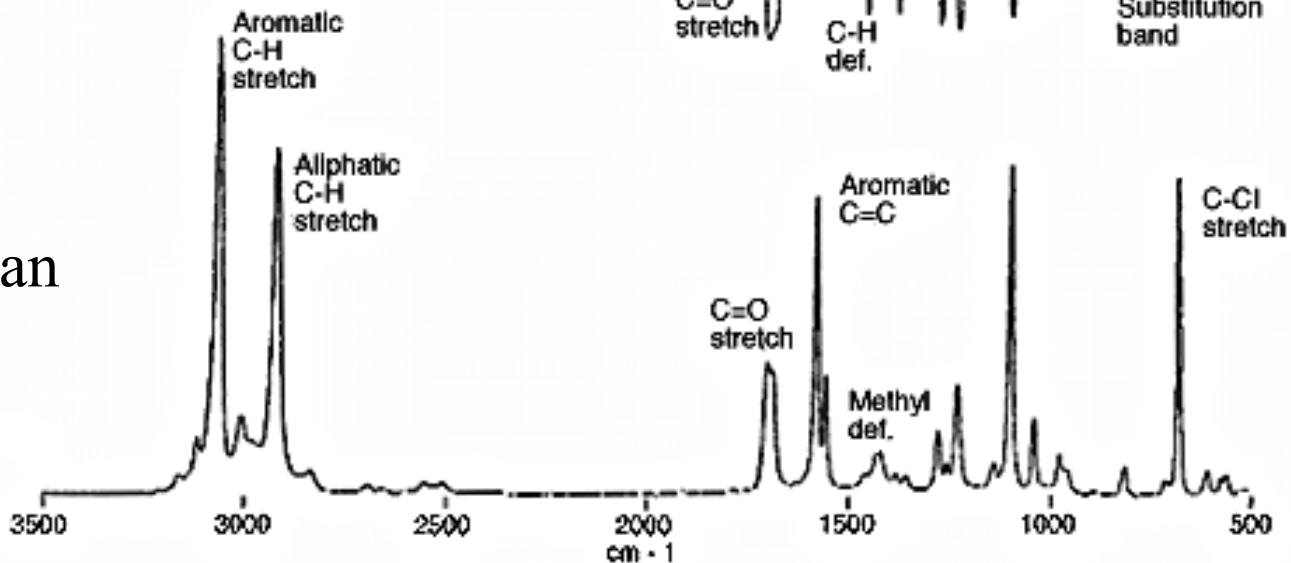


# Raman vs. FTIR

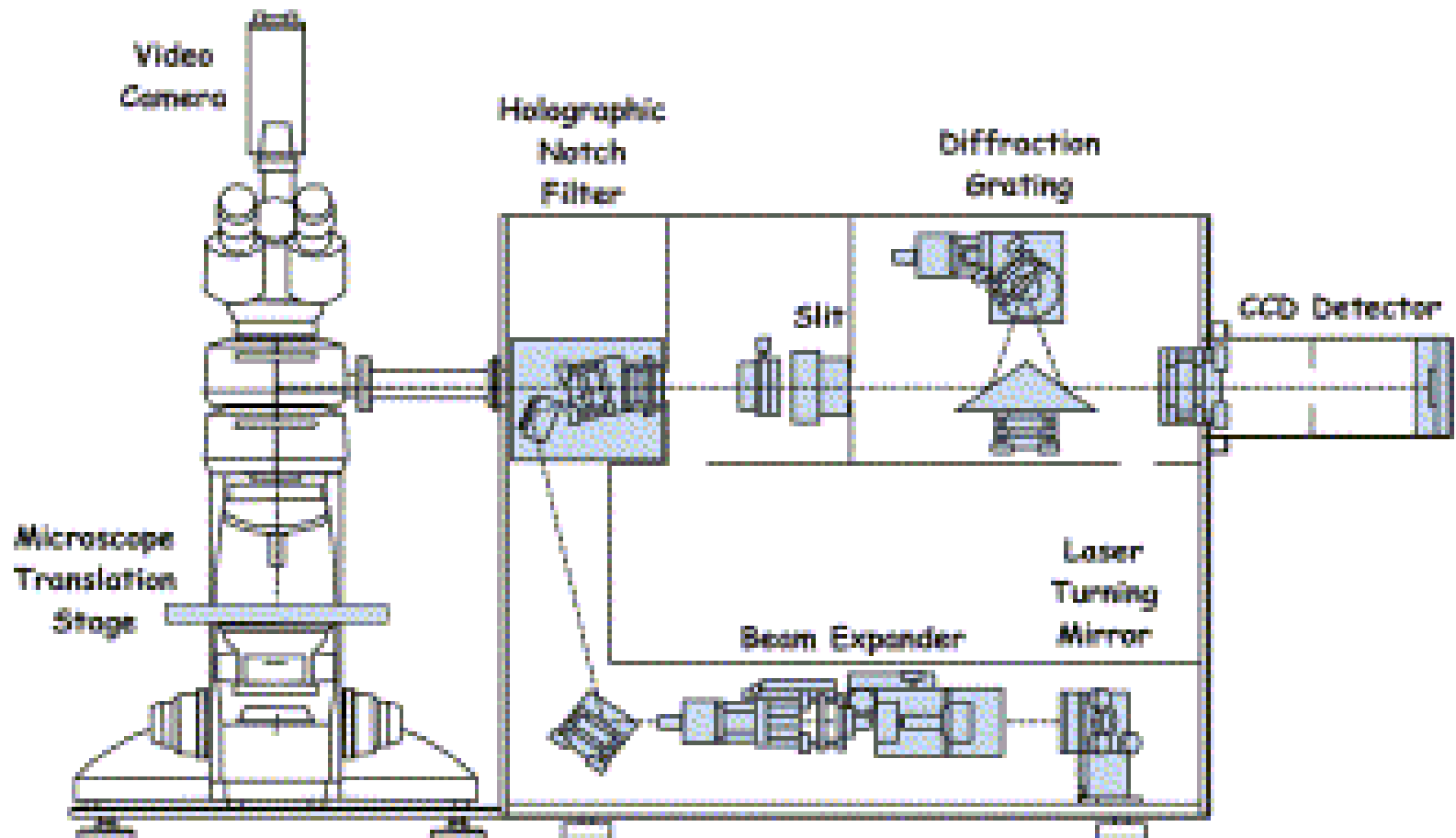
FT IR



(FT) Raman

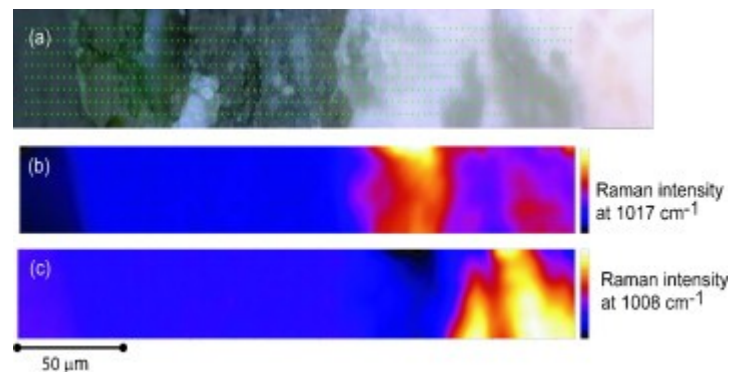
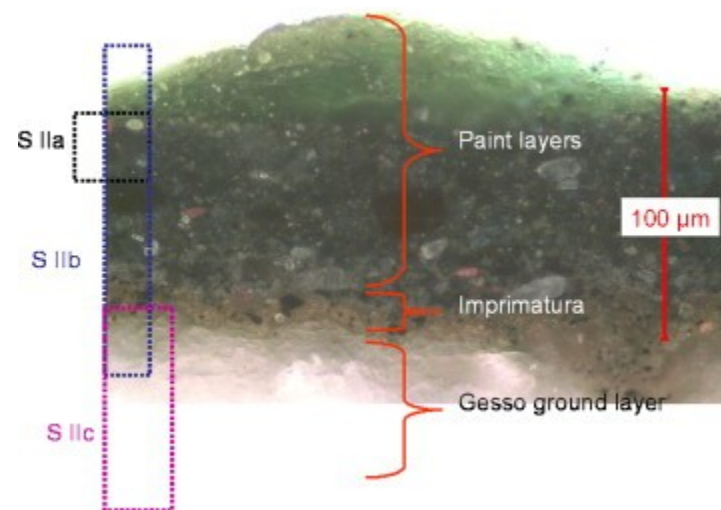


# Ramanova mikroskopie



# Ramanova mikroskopie maleb

*Portrét mladíka* (neznámý severoitalský malíř, cca 1515)

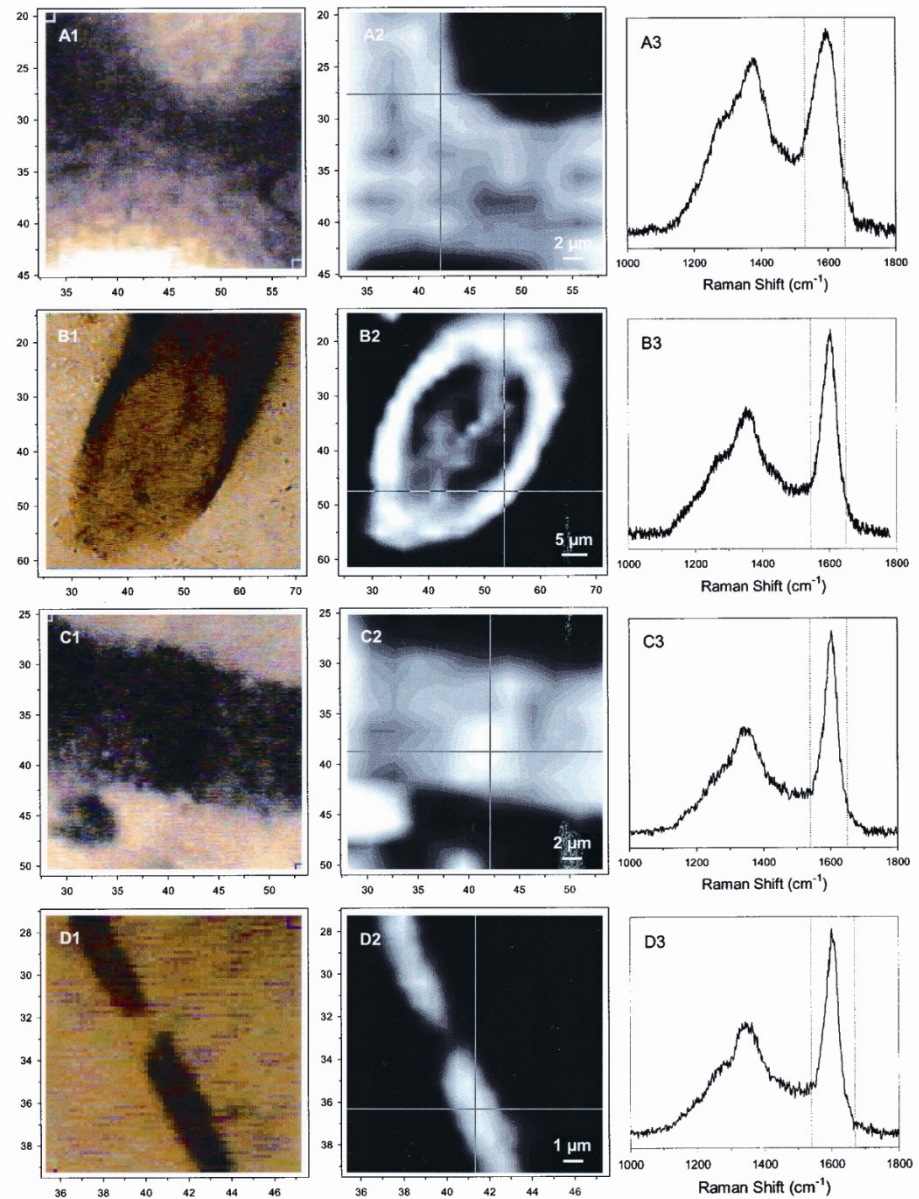


Ramanovské mapy vzorku S IIb.  
(a) optický obraz, (b) anhydrit, (c) sádrovec (gypsum).



# Ramanova mikroskopie

mikrofosilie  
v jurských  
rohovcích

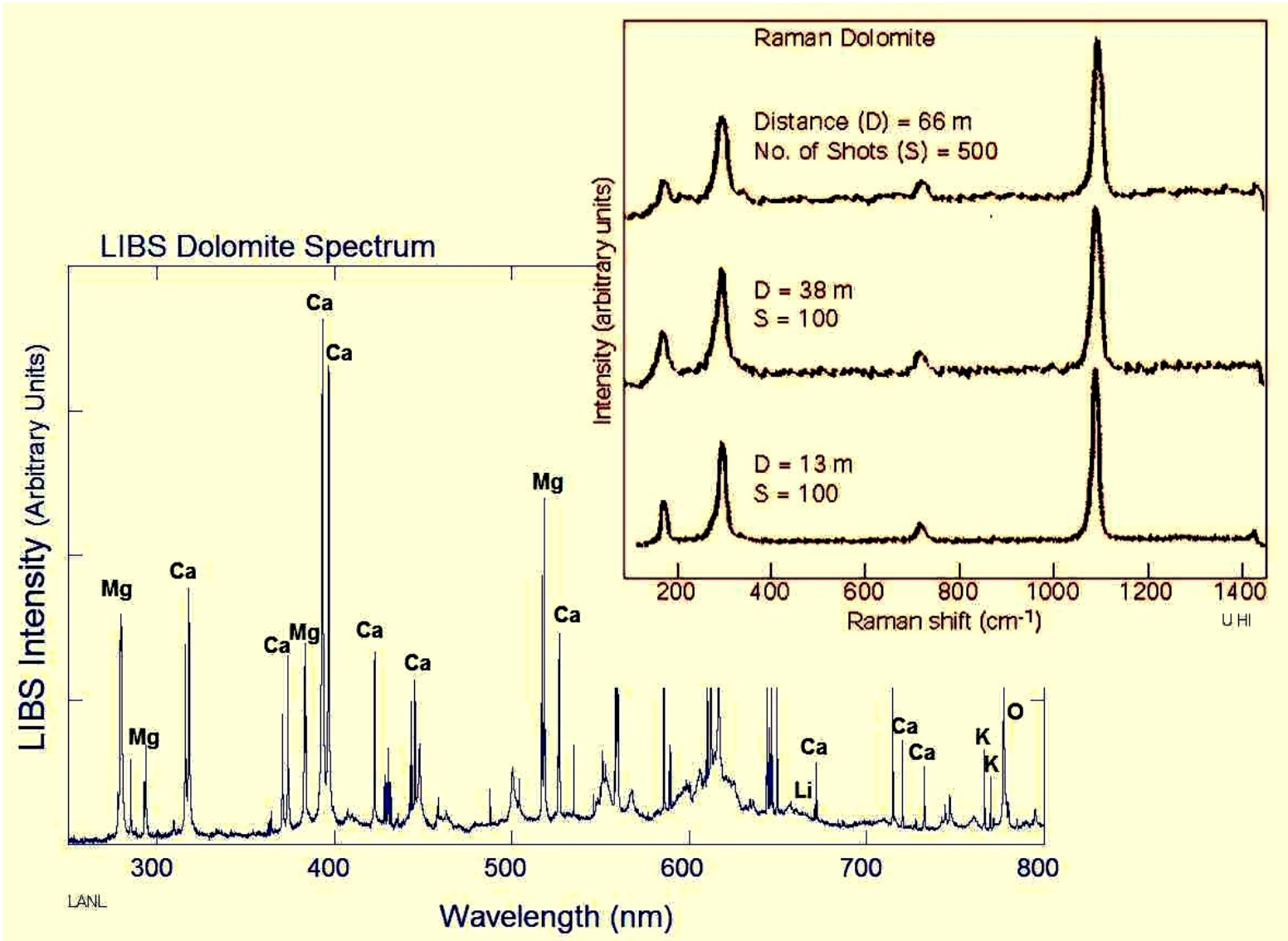


**Fig. 1.** Optical images (column 1), Raman images (column 2), and spectral bands used for Raman imaging (column 3) of permineralized carbonaceous fossils at or near the upper surfaces of polished chert thin sections: (A) Cell wall in the conductive tissue (lignified xylem) of an aquatic fern *Dennstaedtia* from the essentially unmetamorphosed ~45-Ma-old Clarno Formation of Oregon. (B) Tangential section of the tubular sheath of a *Lyngbya*-like oscillatoriacean cyanobacterium in a conical stromatolite (*Conophyton gaubitzia*) from the subgreenschist facies ~650-Ma-old Chichkan Formation of Kazakhstan. (C) Transverse cell wall of a broad cellular trichome (*Gunflintia grandis*), and (D) a narrow prokaryotic filament (*G. minuta*), in domical stromatolites of the greenschist facies ~2,100-Ma-old Gunflint Formation of Ontario, Canada. Each Raman image was produced by combining several hundred pixel-assigned point spectra ("spexels"), like those shown for each specimen in column 3, acquired over a small square part of the total area analyzed. The resolution of the Raman images is defined by the pixel dimensions of their component spexels; for A–C, 2 μm per pixel, and for D, 0.5 μm per pixel.

# Raman + FTIR mikroskopie

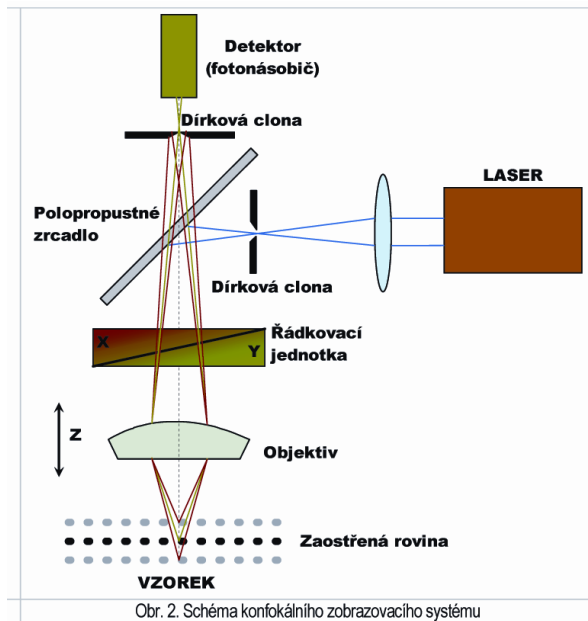


# Kombinace Raman + LIBS

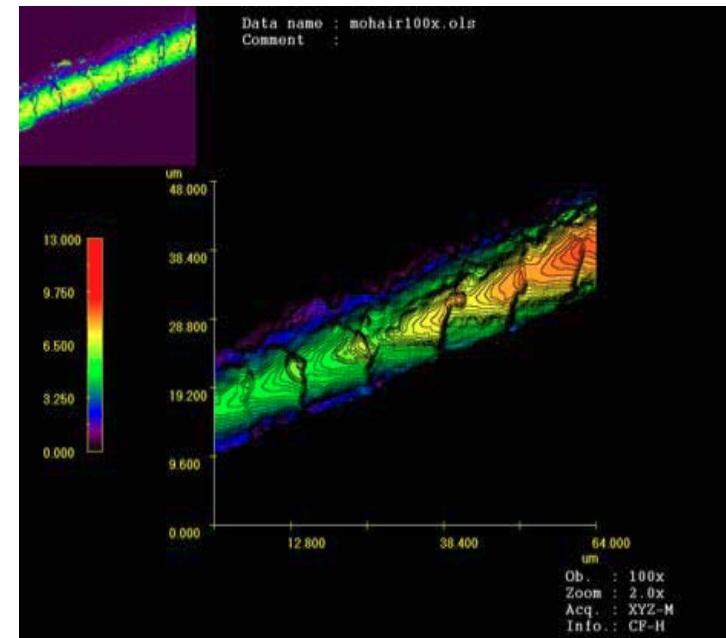
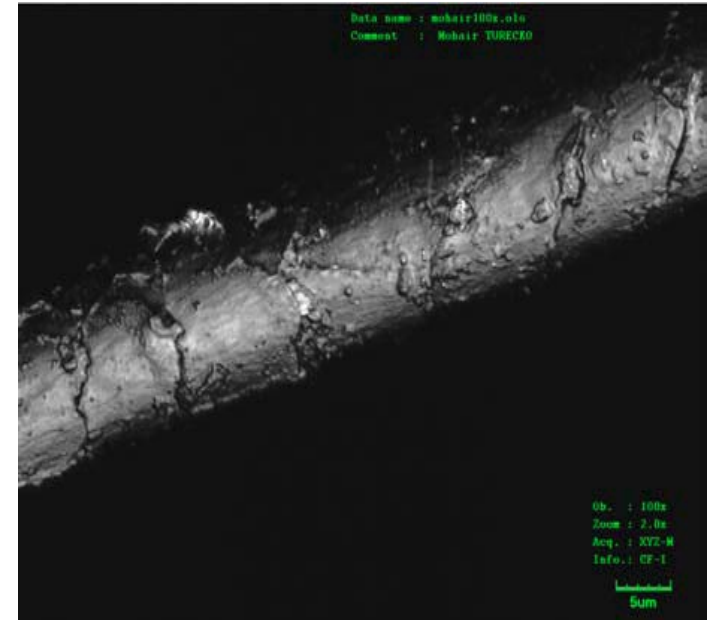


# Konfokální mikroskopie

Světelným zdrojem je laserové záření. Konfokální mikroskop poskytuje mimořádně ostrý, kontrastní, vysoce informativní obraz s vysokým rozlišením. Struktury nacházející se nad a pod rovinou fokuse nemají téměř žádný vliv na kvalitu obrazu. Hloubka ostrosti je vždy minimální.



CM 3D Mikroskopický snímek vlákna mohérové vlny (Turecko) – objektiv 100x a 2násobný zoom



# Konfokální Ramanova mikroskopie

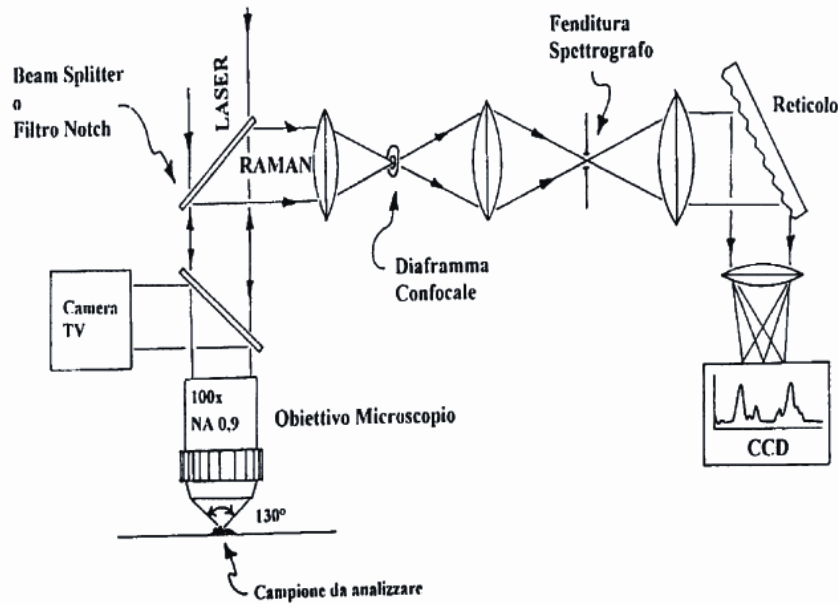
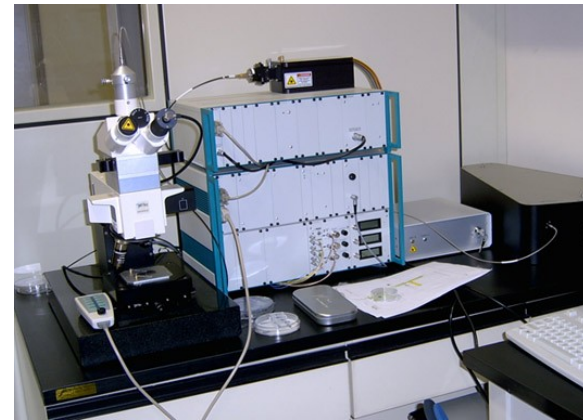
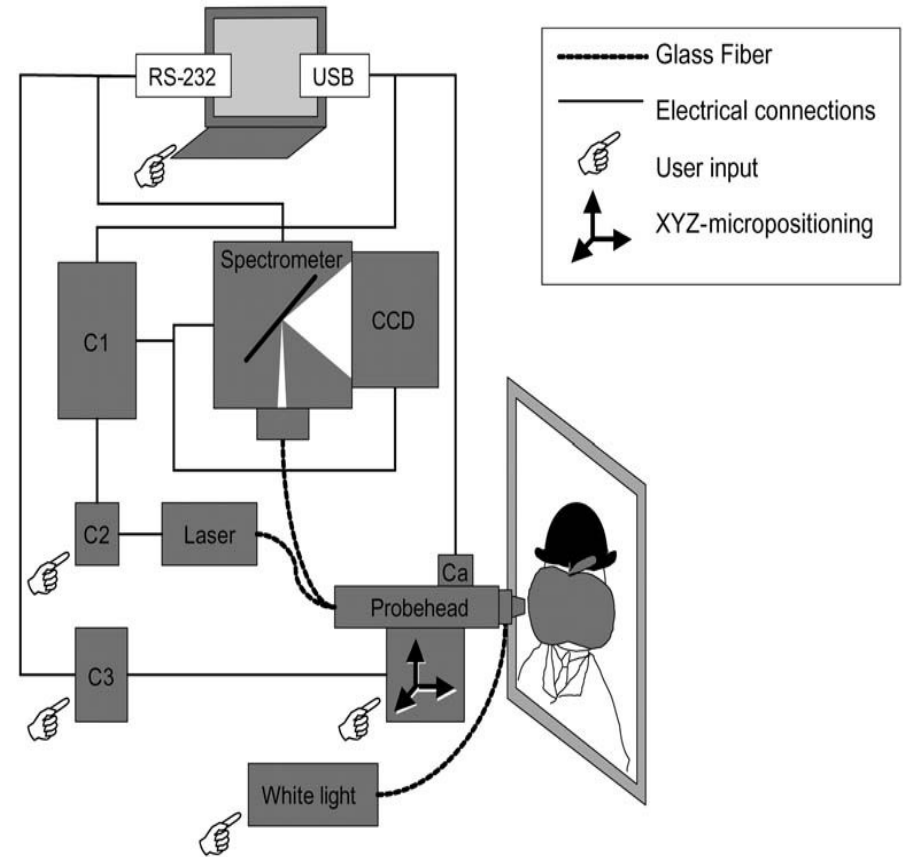


Figure 3. Scheme of confocal Raman apparatus.



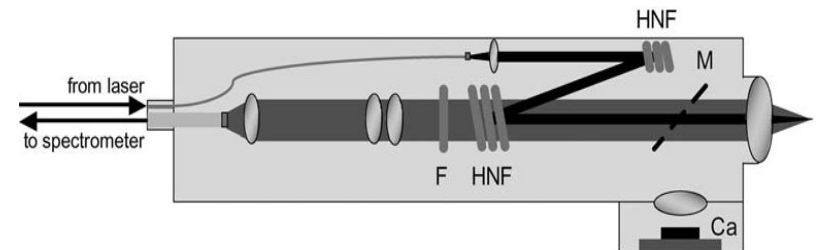
# Mobilní zařízení pro Ramanovu spektrometrii

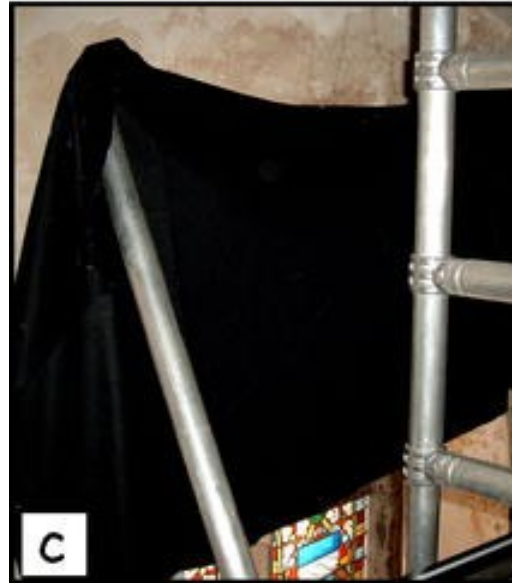
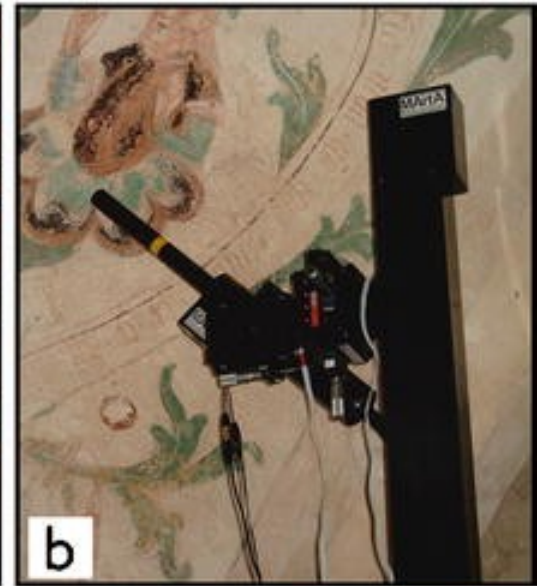


*M* : 95% propustné zrcadlo pro vizualizaci plochy kamerou (*Ca*).

*HNF* : holografické filtry odrážející laserový paprsek a propouští ramanovsky posunuté záření (Stokes)

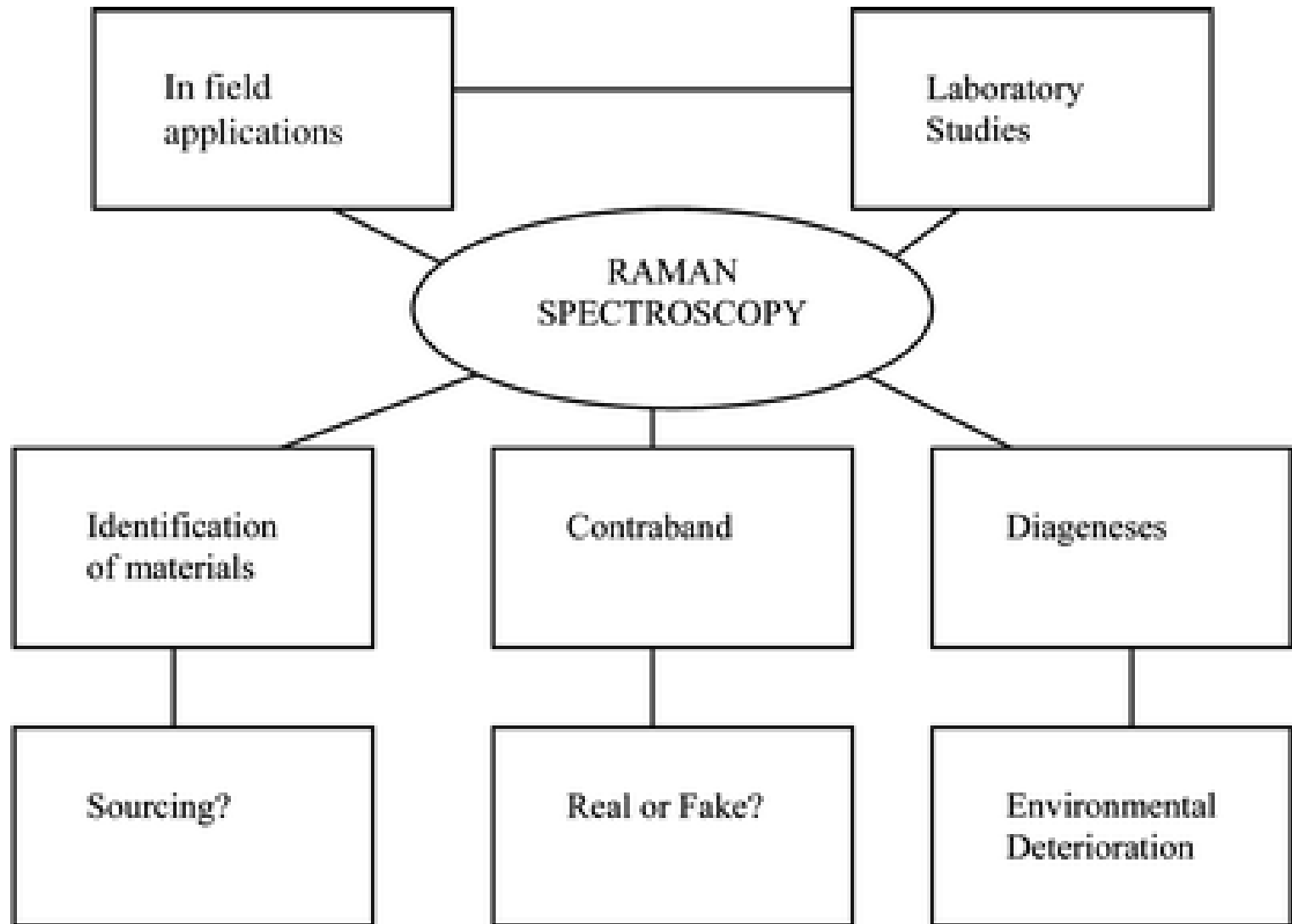
*F* filtry pro anti-Stokesovskou část spektra





Analýza nástěnných maleb (kaple Ponthoz.)

# Aplikace Ramanovy spektrometrie

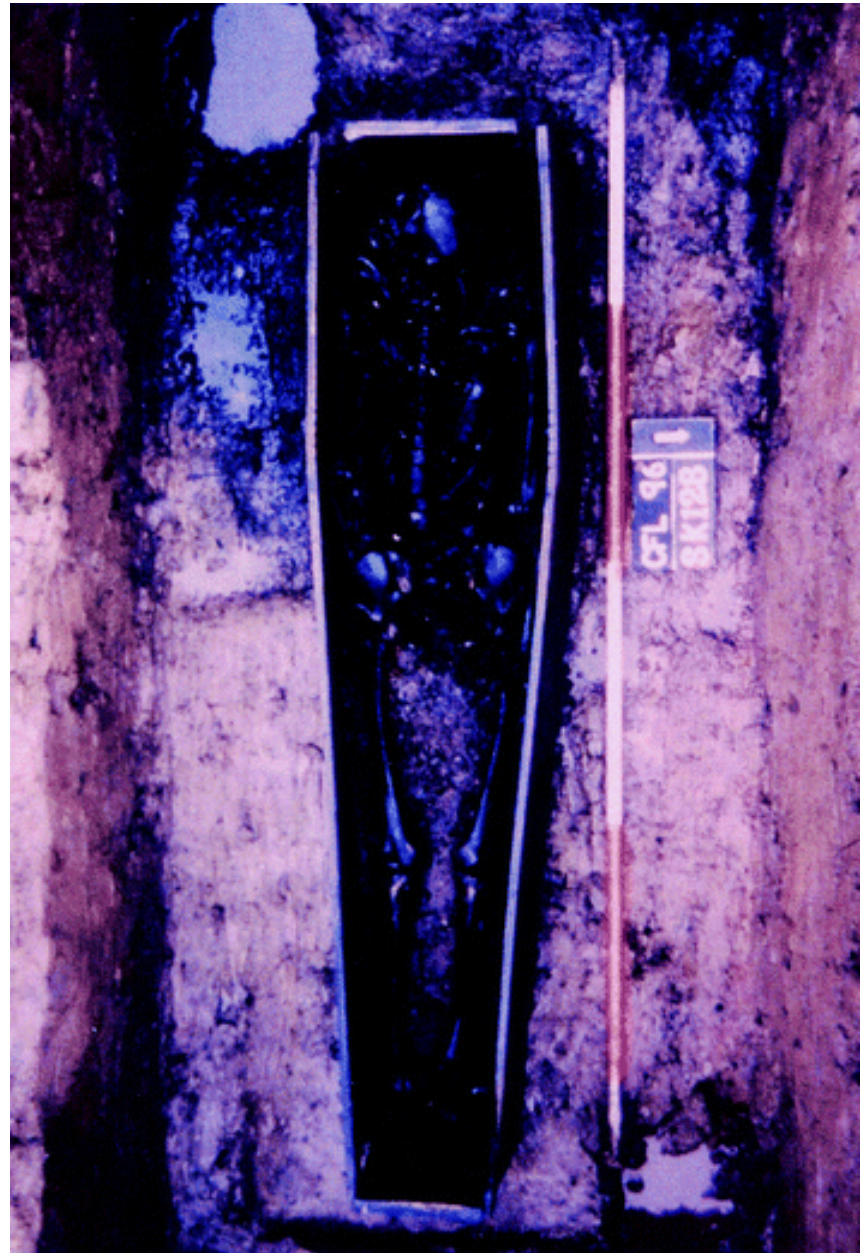


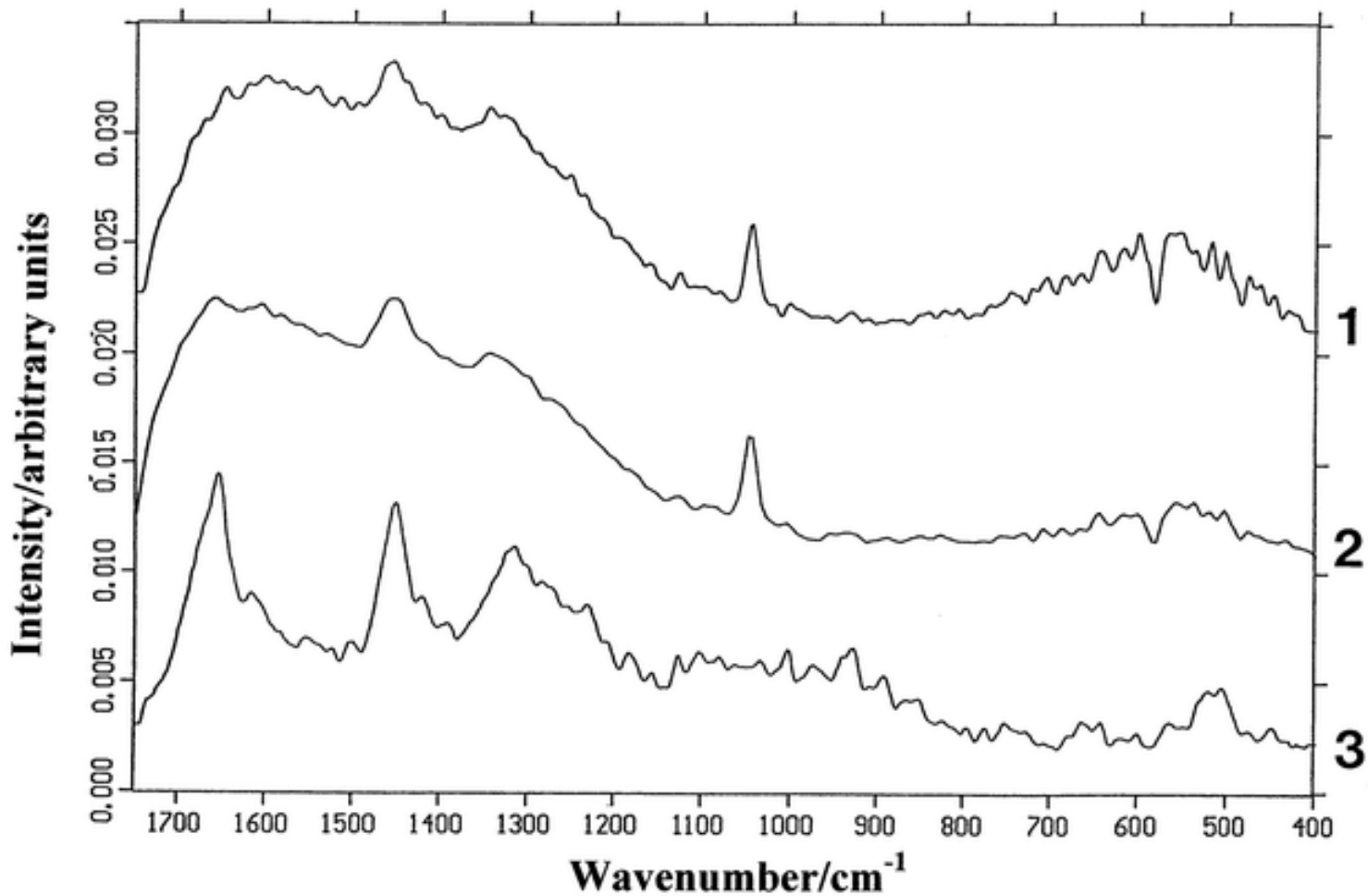


# Analýza lidských pozůstatků

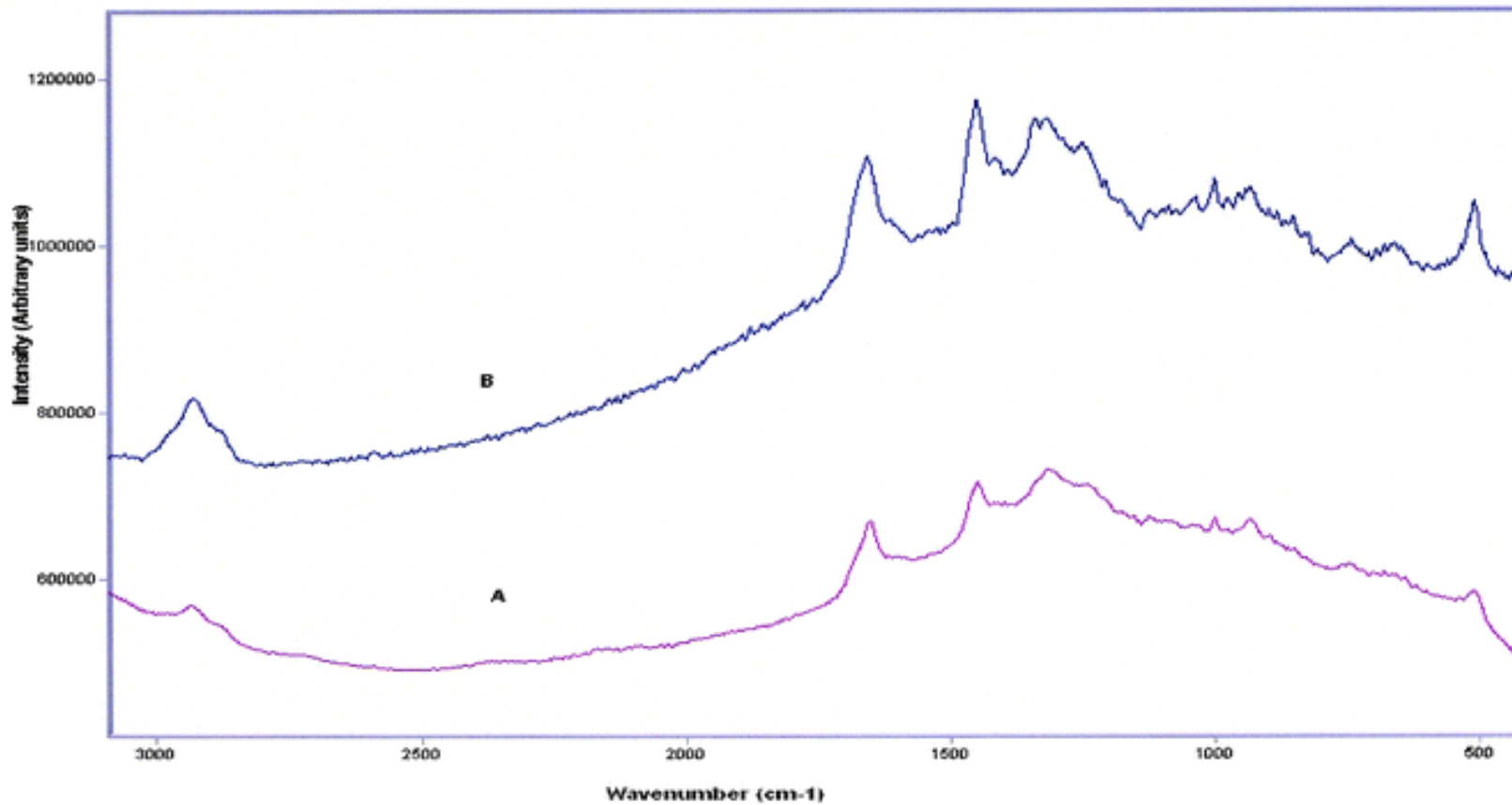
## Analýza vlasů

Kosterní pozůstatky z výzkumu z  
Newcastlu (silně podmáčená  
lokalita): měkké tkáně rozloženy,  
zachovaly se vlasy.



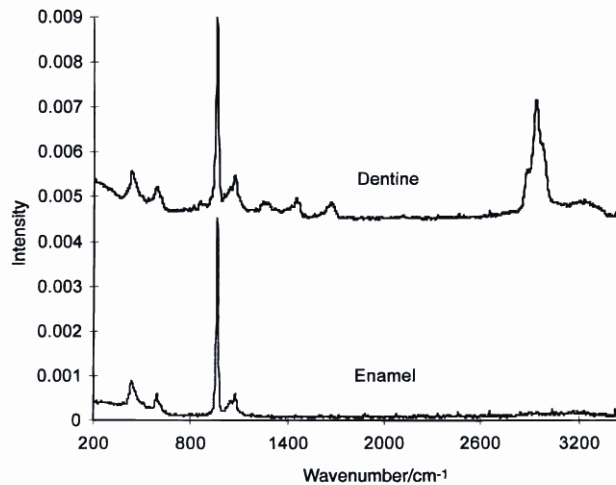


Ramanova spektra vlasů z lidského skeletu (pozorována degradace keratinové tkáně), přítomnost pásu 1050 cm<sup>-1</sup> ve spektrech 1 a 2 (archeologické vzorky) je charakteristický pro PbCO<sub>3</sub>, pravděpodobně z olověné rakve. Vzorek 3 moderní, tmavé vlasy.

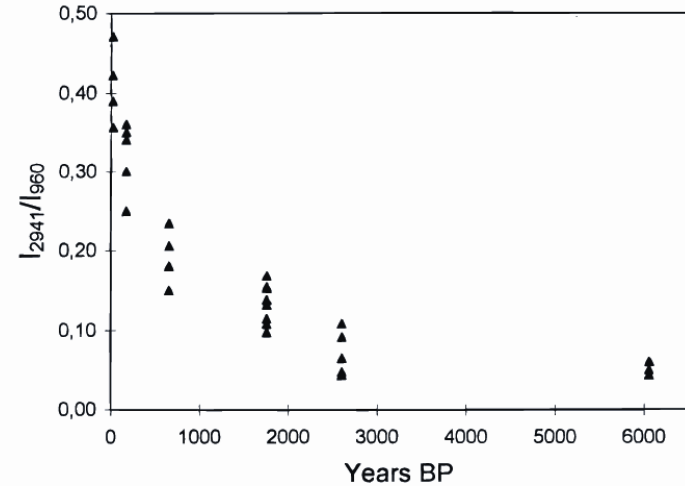


Ramanova spektra historických vzorků vlasů ve vynikajícím stavu zachování: Robert Stephenson (1859). *A* spektrum Stephensonových blond vlasů, *B* moderní blond vlasy.

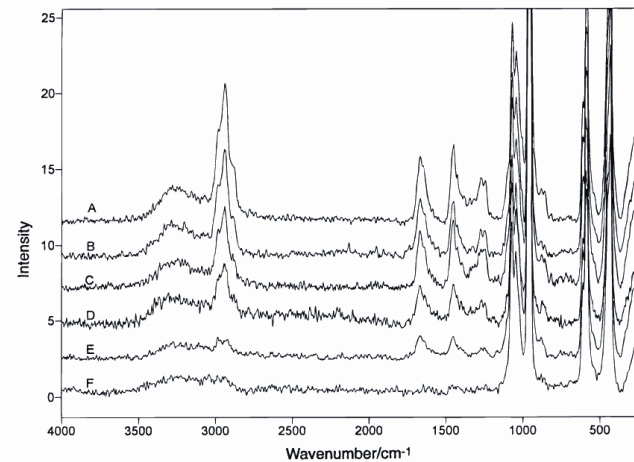
# Analýza zubů



**Figure 1.** Typical FT-Raman spectra of human tooth enamel & dentine of a transverse section of a human tooth. 1064 nm excitation;  $4 \text{ cm}^{-1}$ ; 120 mW power; 4000 scans.



**Figure 4.**  $I_{2941}/I_{960}$  relative intensities as a function of the tooth burial period.



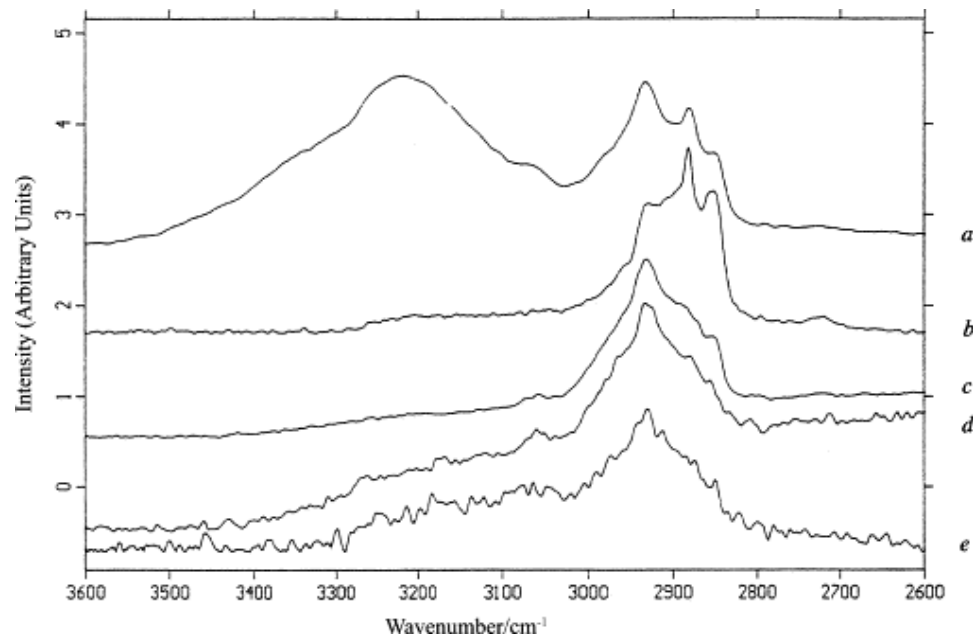
**Figure 3.** FT-Raman external enamel normalized spectra of the teeth examined: (A) Bologna, Italy, 0 BP; (B) Sassari, Italy, 150 BP; (C) S. Agata, Ravenna, Italy, 650 BP; (D) Bagnacavallo, Italy, 1700 BP; (E) Monte Casasia, Italy, 2700 BP; (F) Passo di Corvo, Foggia, Italy, 5800–6300 BP.

# Analýza mumifikovaných tkání



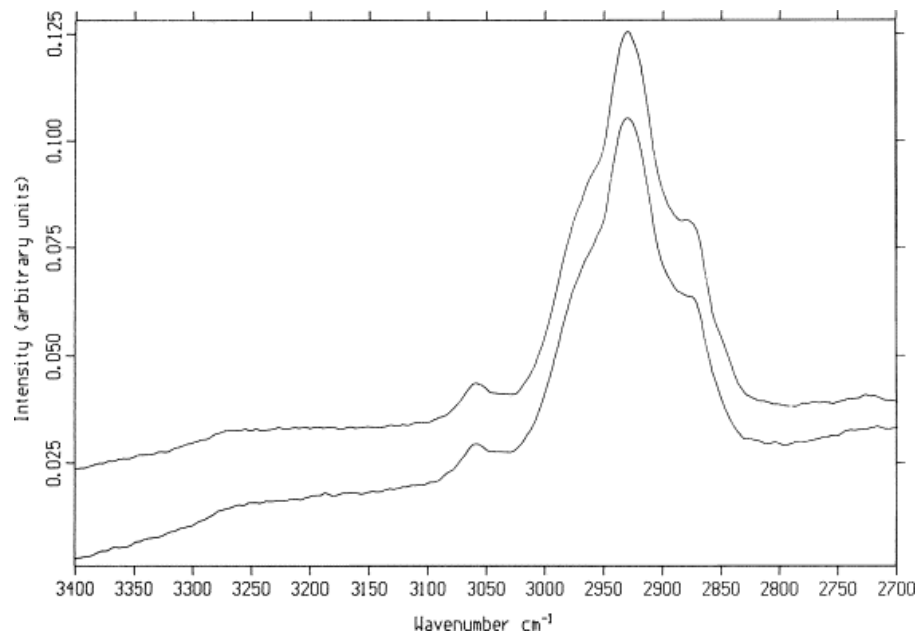
## FT-Raman spektra

- (a) současná lidská kůže (stratum corneum),
- (b) stratum corneum ledovcového muže Ötziho,
- (c) peruánská světle-pigmentovaná mumie,
- (d) grónská mumie (30-letá žena)
- (e) peruánská tmavě-pigmentovaná mumie.



## FT-Raman spektra

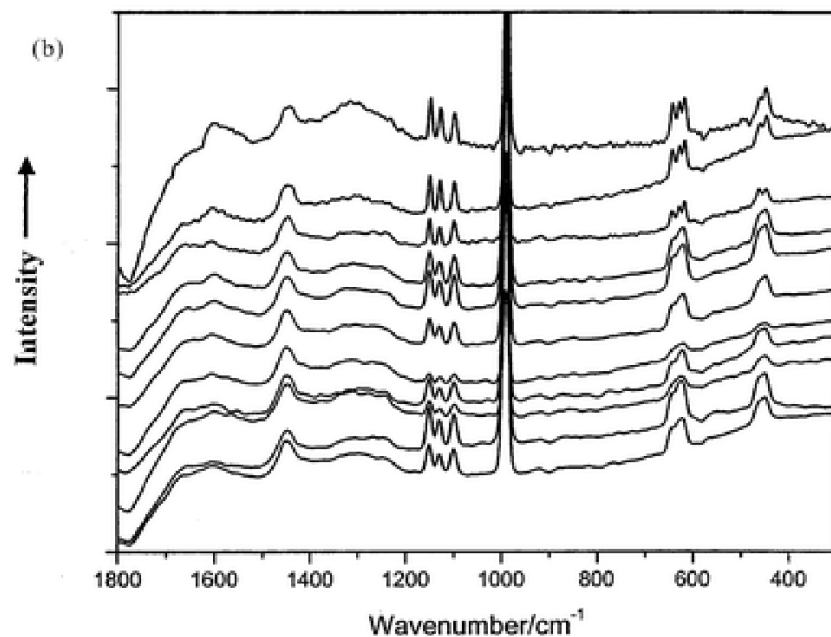
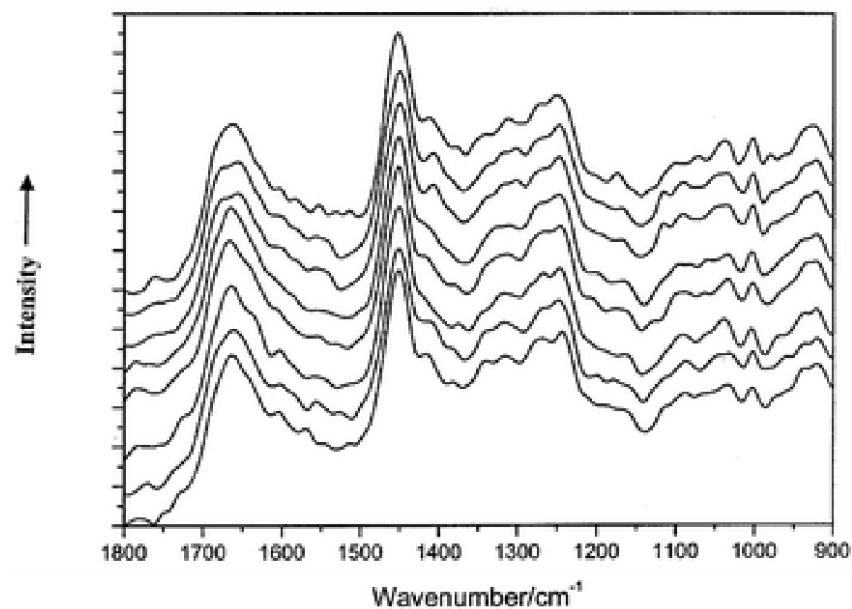
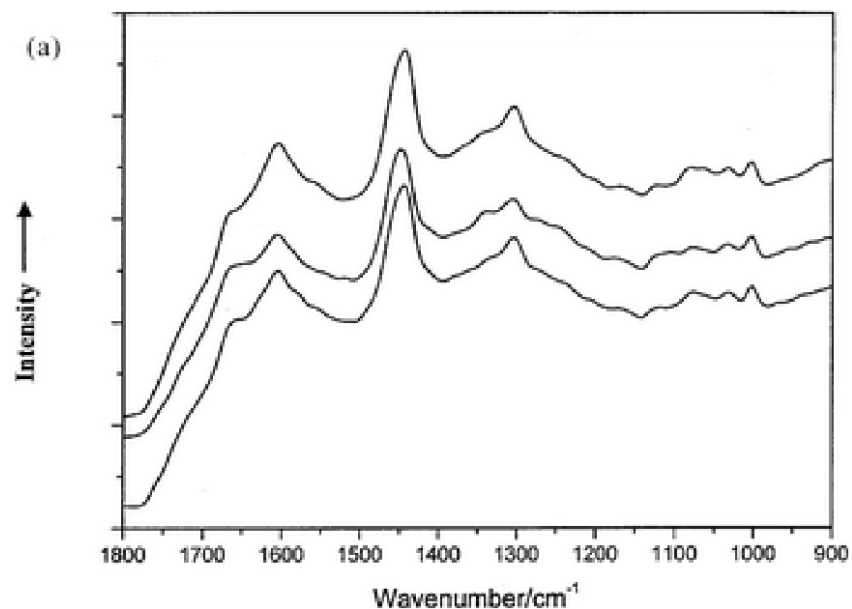
- moderní dětský nehet (nahore)
- nehet mumifikovaného dítěte (Grónsko) (dole)



# Umělá mumifikace



Sarkofágy mumii Khnum-Nakhta a Nekht-Ankha (12. dynastie, cca. 2000 BC).



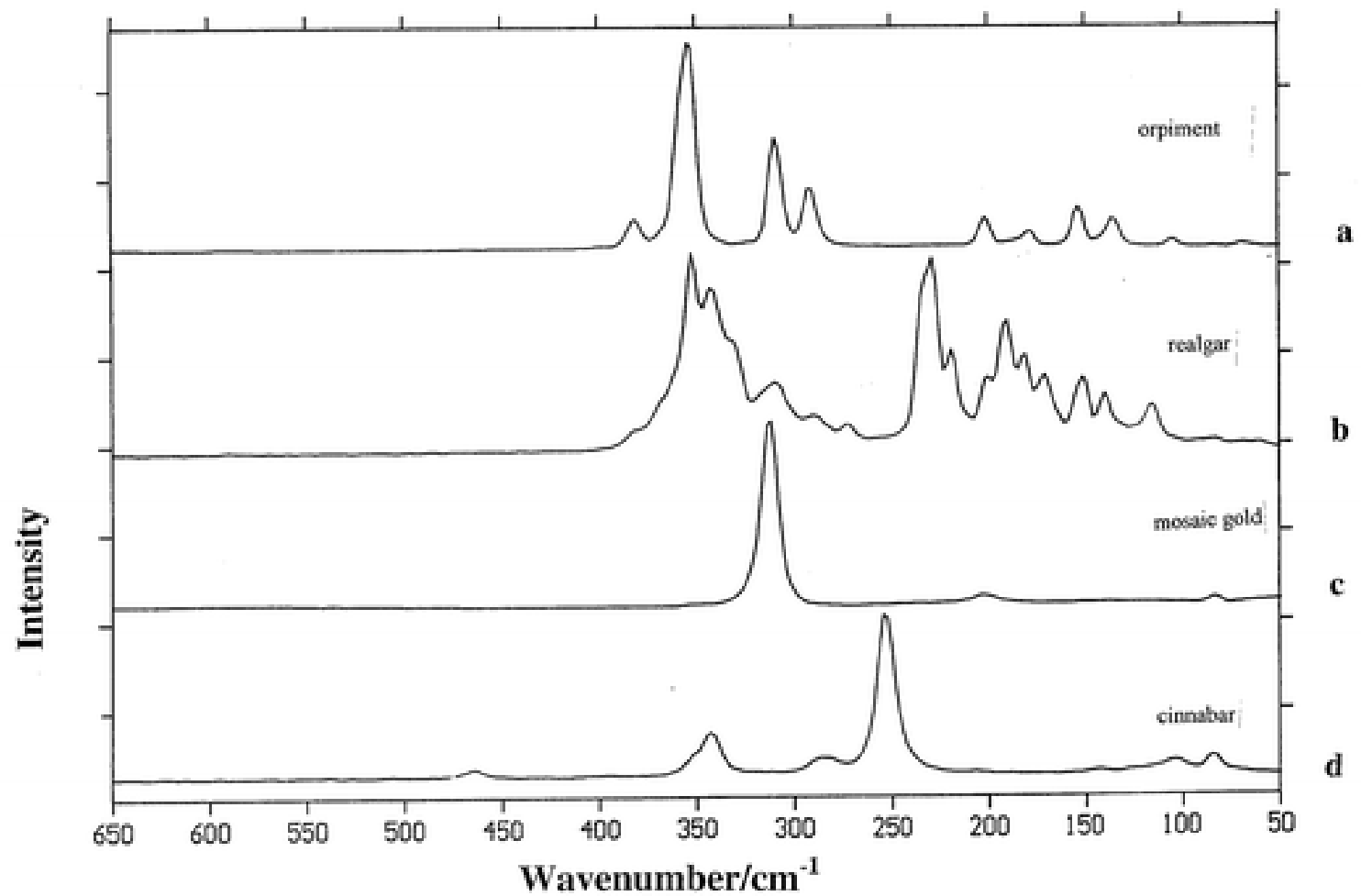
Ramanova spektra mumifikované kůže Nekht-Ankha v různém stavu zachování (a) *nahore*, špatně dochovaná, (a) *dole*, dobře zachovaná a (b) vzorek obsahující mumifikační substanci – síran sodný (*natron*). Zajímavé je špatné zachování kůže v místech přítomnosti mumifikační chemikálie.



# Ramanova spektrometrie pigmentů

Polychromovaná socha sv. Anny v Santa  
Maria la Real, Sasamon, Španělsko (13.  
stol.).





Ramanova spektra auripigmentu ( $\text{As}_2\text{S}_3$ ), realgaru ( $\text{As}_4\text{S}_4$ ), mozaikového zlata ( $\text{SnS}_2$ ) a rumělky ( $\text{Hg S}$ ).

# Oltář ze “San Antolín y San Bernabé”

<i>Pigment</i>	<i>Chemical formula</i>	<i>Raman bands <math>cm^{-1}</math></i>
<b>Vermilion</b>	HgS	255, 309, 347, 376
<b>Azurite</b>	$2CuCO_3 \cdot Cu(OH)_2$	251, 404, 623, 770, 838, 1098
<b>Malachite</b>	$CuCO_3 \cdot Cu(OH)_2$	153, 168, 179, 223, 272, 352, 435, 516, 538, 722, 755, 1062, 1100, 1372, 1496
<b>Lead White</b>	$PbCO_3$	409, 1054
<b>Lapislazuli</b>	$Na_8[Al_6Si_6O_{24}]S_n$	258, 286, 545, 581, 802, 1097, 1358, 1642
<b>Massicot</b>	PbO	286, 384, 419
<b>Gypsum</b>	$CaSO_4 \cdot 2H_2O$	182, 216, 416, 495, 623, 673, 1009, 1140

Table 1. Chemical formula and Raman band observed (in  $cm^{-1}$ , wavenumber) of the identified pigments.

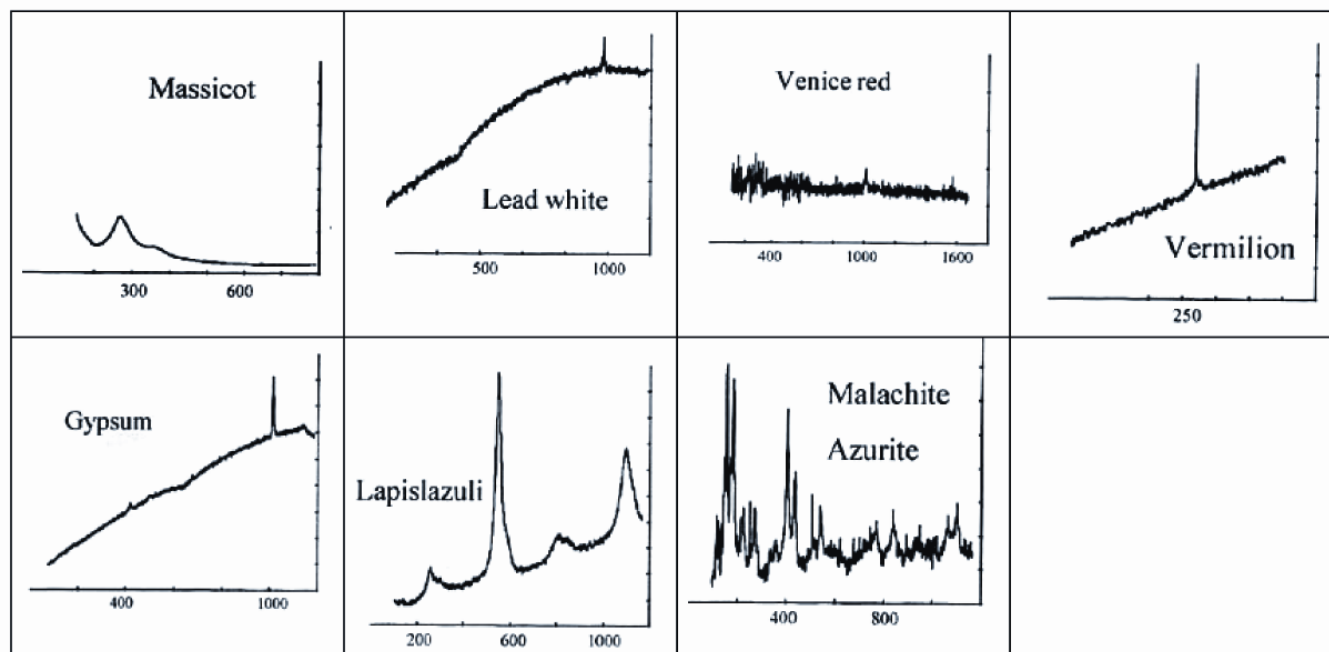
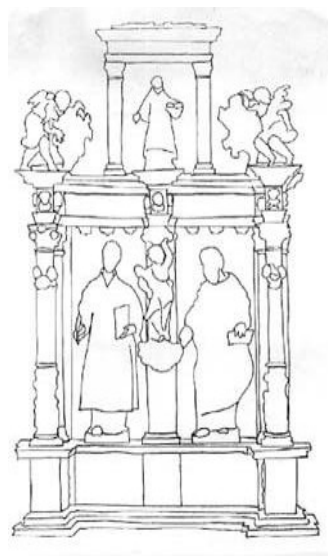
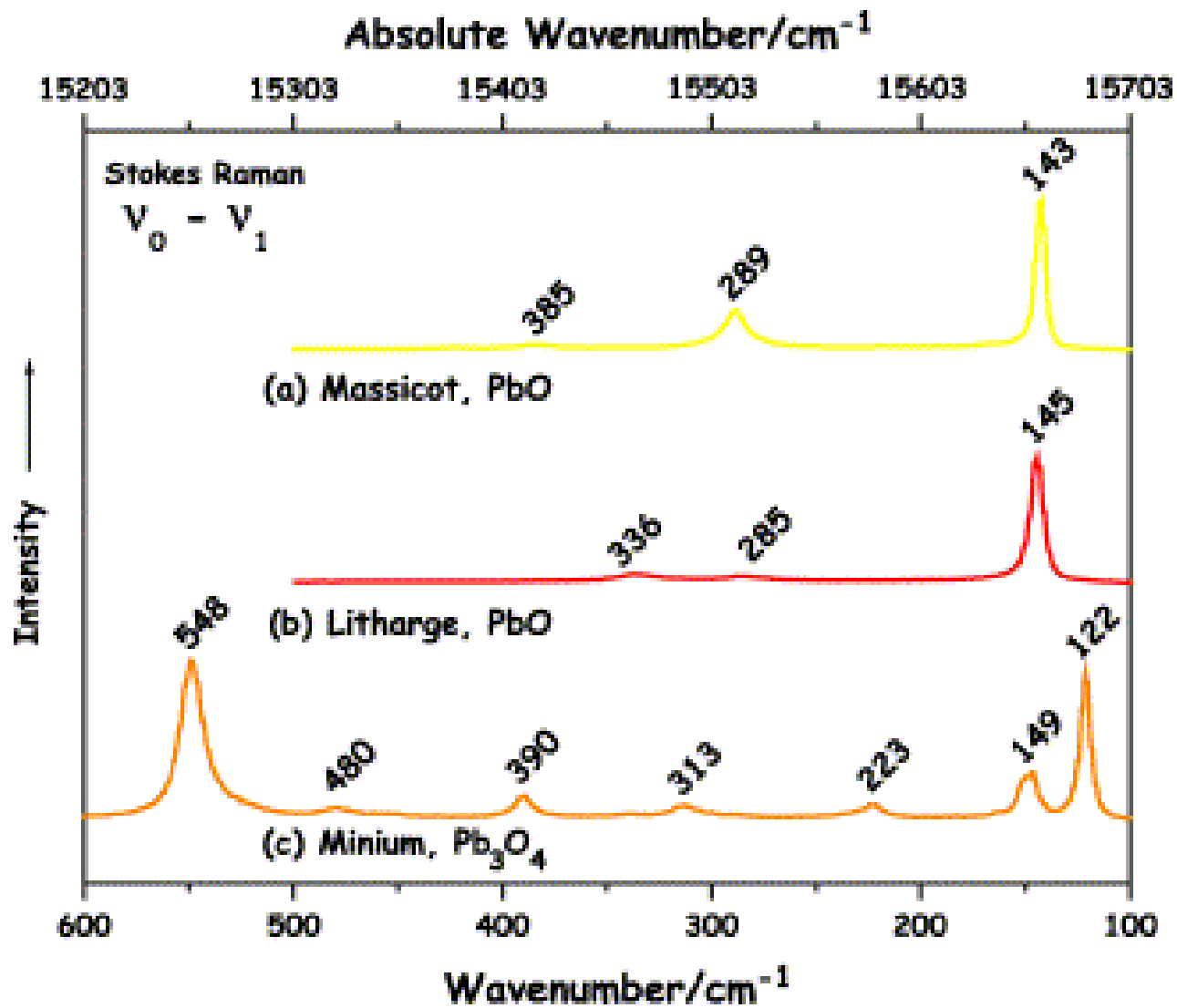


Fig. 5. The Raman spectra of the pictorial materials obtained from the “San Antolín y San Bernabé” altarpiece. The axis are Raman intensity and wavenumber ( $cm^{-1}$ ).



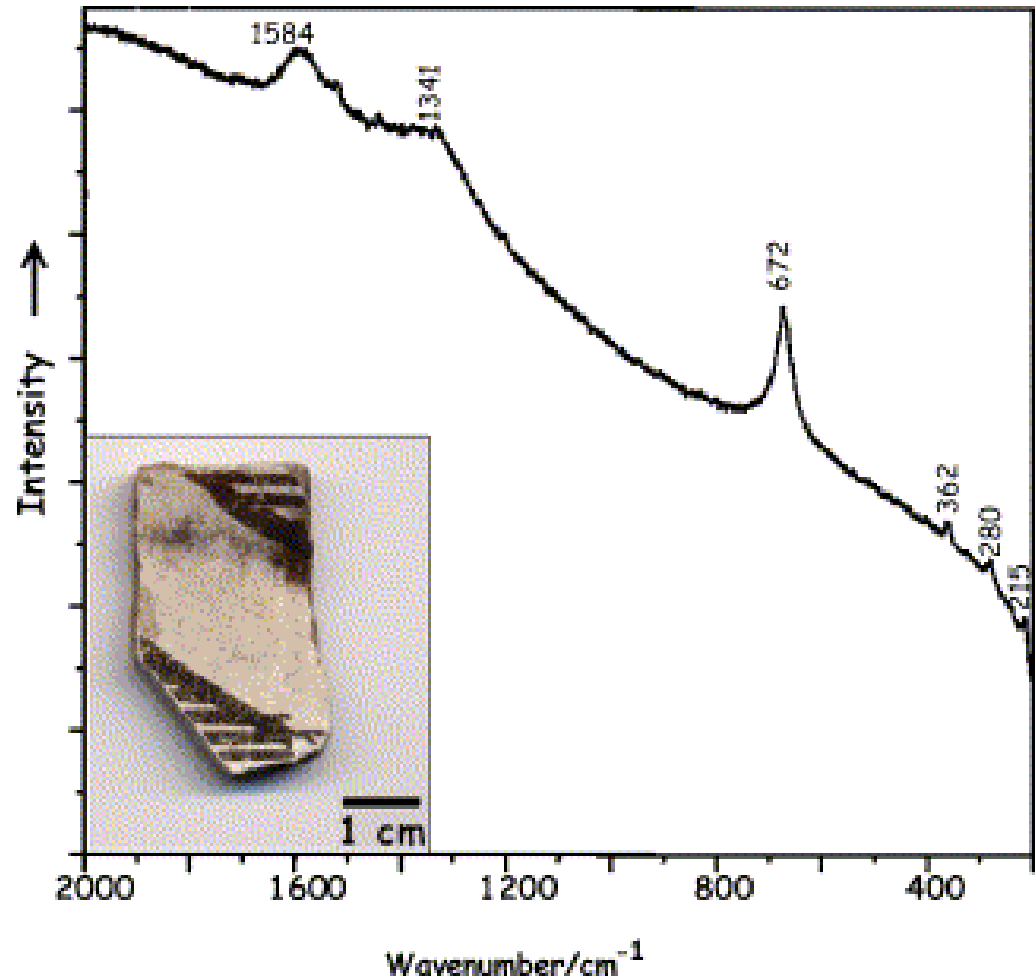
Ramanova spektra (a) orthorhombický masicot, (b) tetragonal klejt (both PbO), (c) suřík (Pb<sub>3</sub>O<sub>4</sub>).

# Identifikace pigmentů na keramice

Ramanovo spektrum černé malby na černobílého střepu (Ancestral Puebloan) z Wallace Ruin, Colorado.

saze, „carbon black“ (1584 a 1341  $\text{cm}^{-1}$ )

magnetit (hlavní pás při 672  $\text{cm}^{-1}$ )

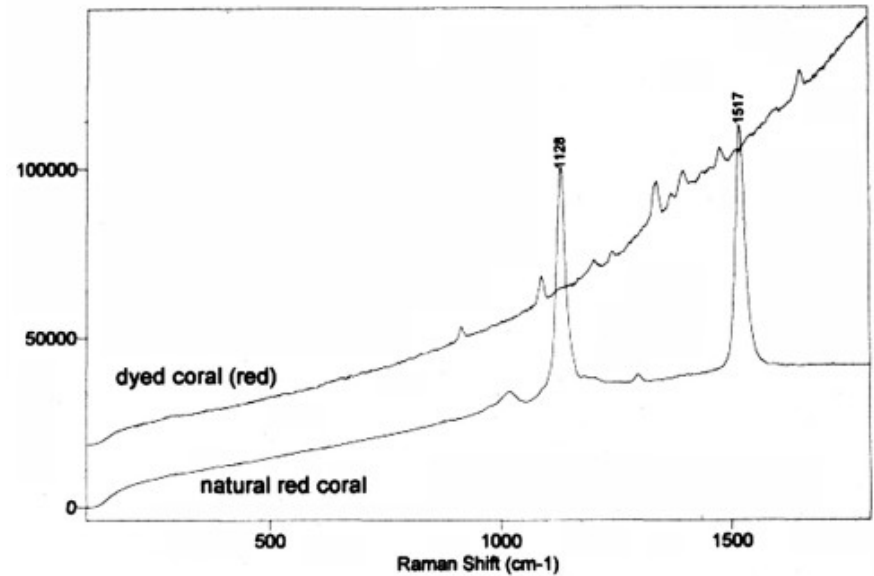
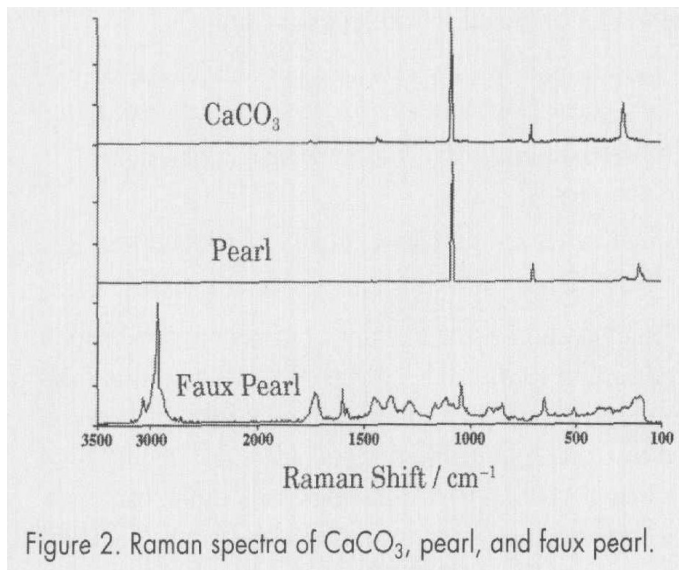


# Rozpoznání imitací

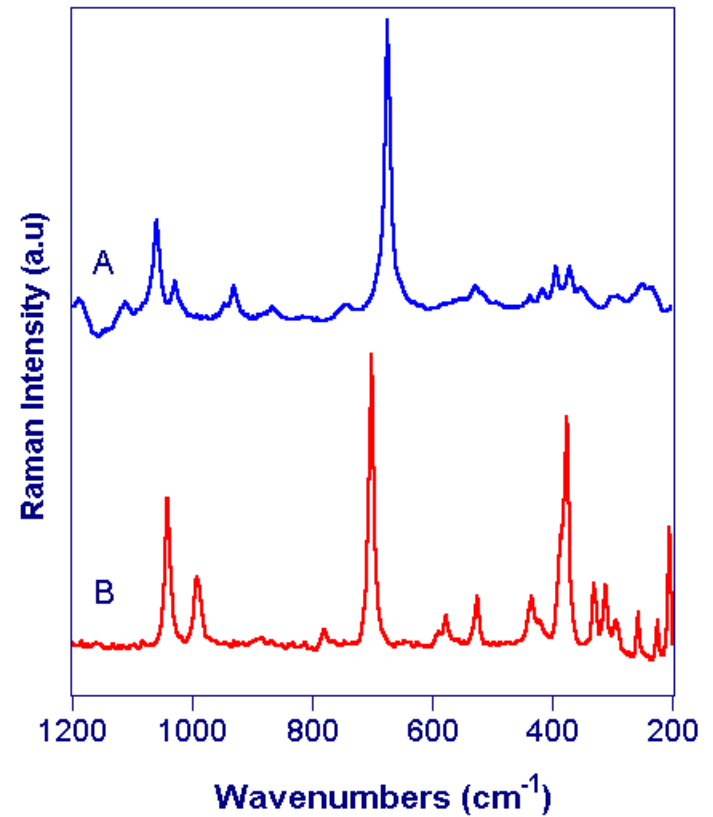
Přírodní barevné korály (karoten)

Barvené korály

Imitace korálů



# Identifikace drahých kamenů



Nefrit -  $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

Jadeit -  $\text{NaAlSi}_2\text{O}_6$

# Identifikace slonoviny



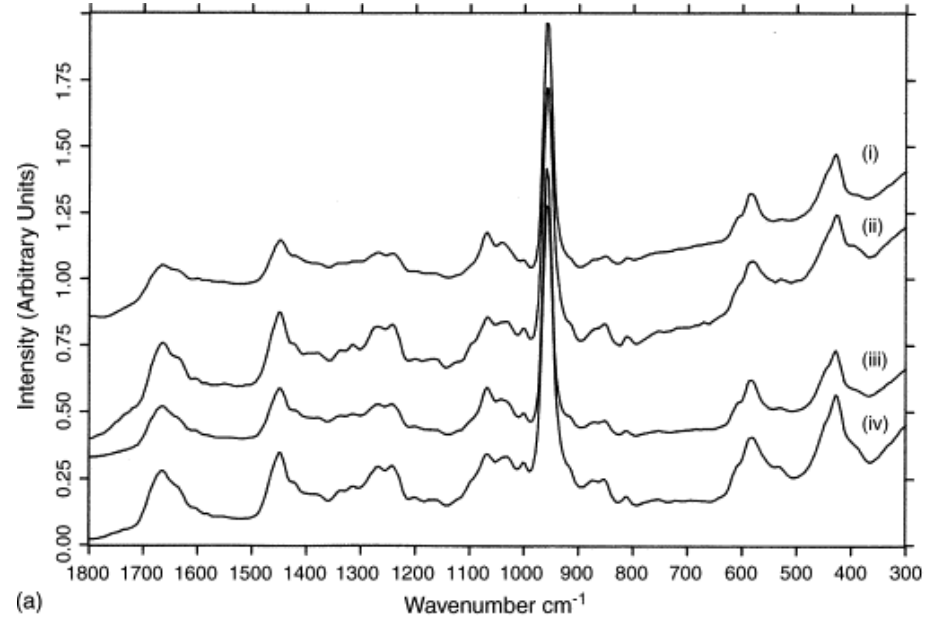
*FT-Ramanova spektra:*

Římské pečtidlo (i)

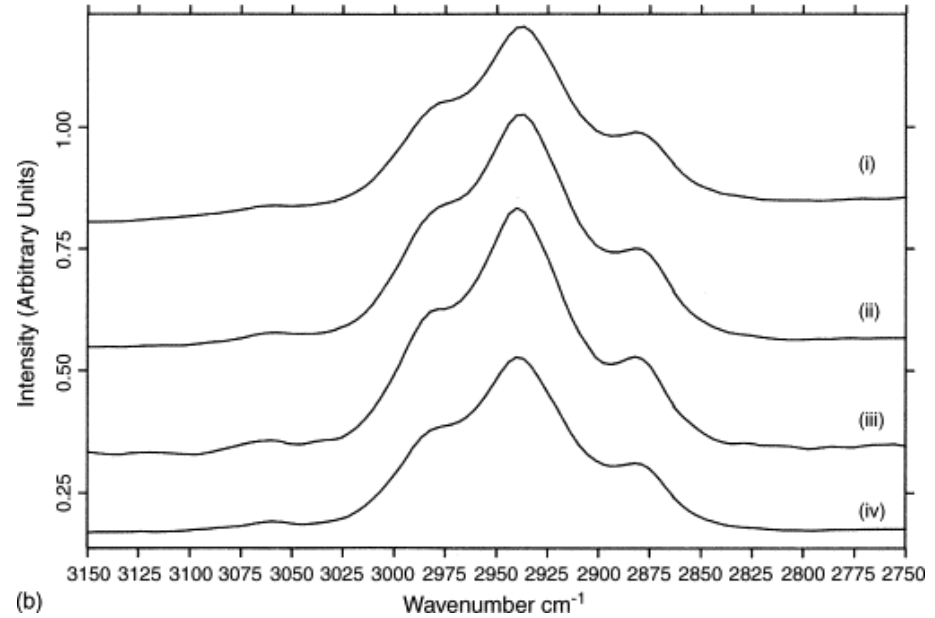
africký slon (ii),

vorvaň (iii)

hroch (iv)



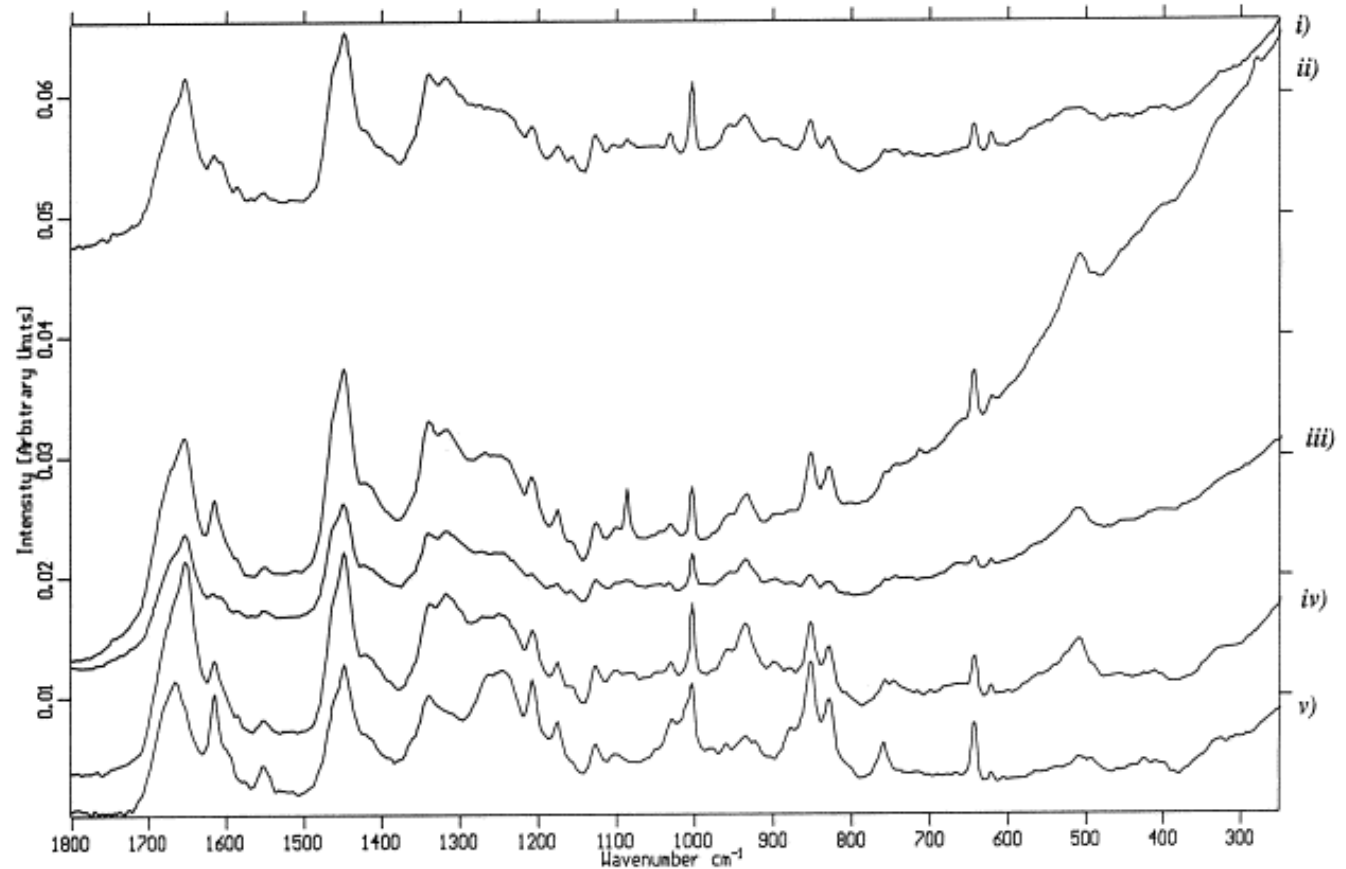
(a)



(b)



# Identifikace rohoviny (keratinů)



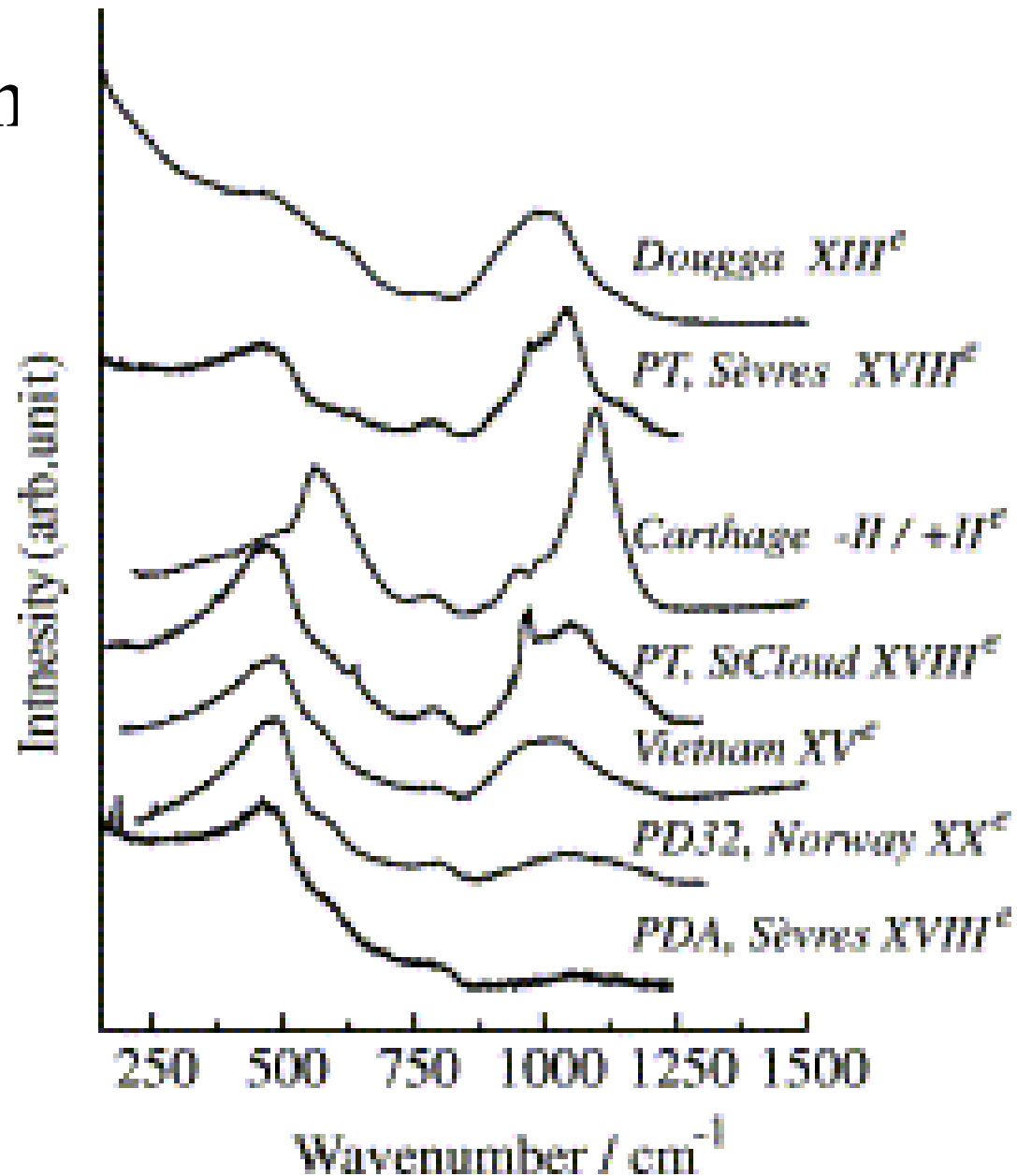
*FT-Ramanova spektra: (i) kopyto, (ii) roh kudu, (iii) nehet, (iv) kravský roh, (v) želví krunýř*

# Glazury a porcelán



*Ramanova spektra glazur/skel:*

Dougga (Ifriqiya), měkký porcelán Sèvres, kartaginské korálky, měkký porcelán St-Cloud, vietnamský porcelán Chu Dâu, moderní Norwichský tvrdý porcelán, tvrdý porcelán Sèvres.

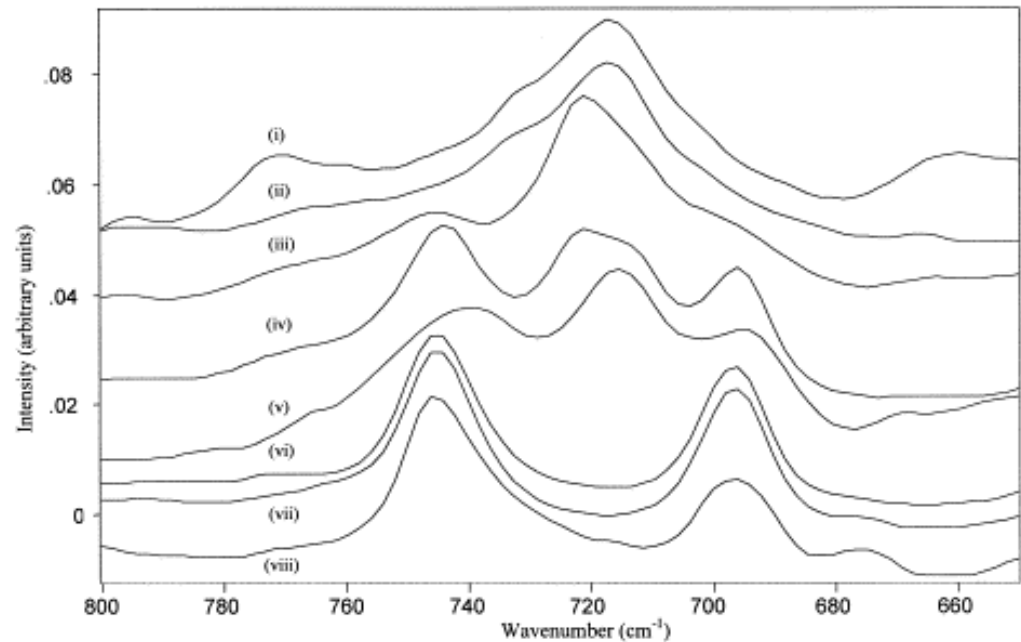
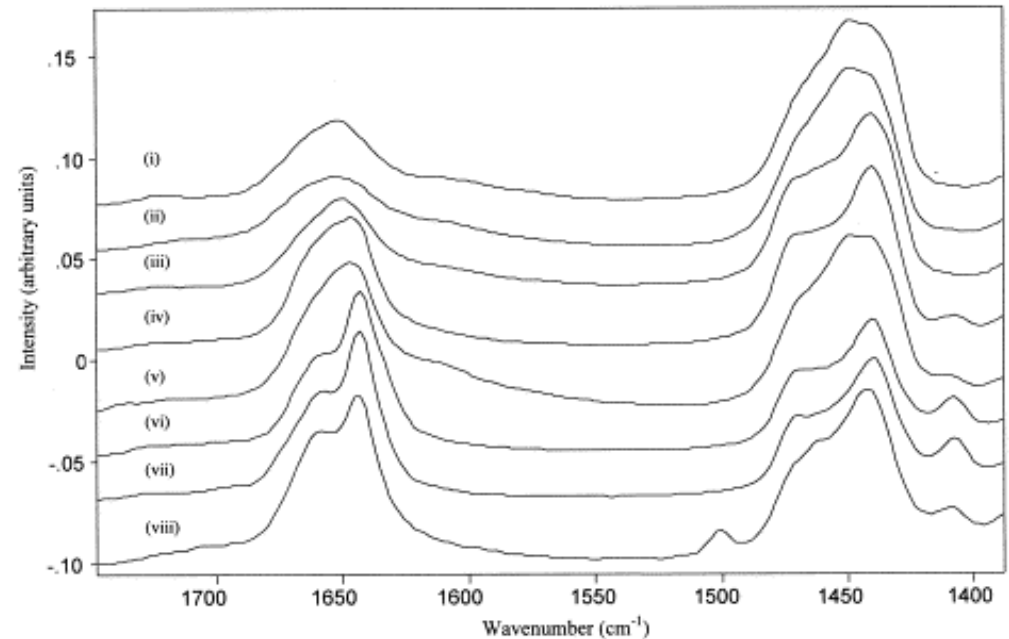


# Identifikace fosilních pryskyřic



*Fosilní pryskyřice:*

(i) Barma, (ii) Libanon, (iii) Mexiko, (iv) Dominikánská republika, (v) V pobřeží Anglie, (vi) V Afrika, (vii) Kolumbie, (viii) S Německo.





dammara



sandarac

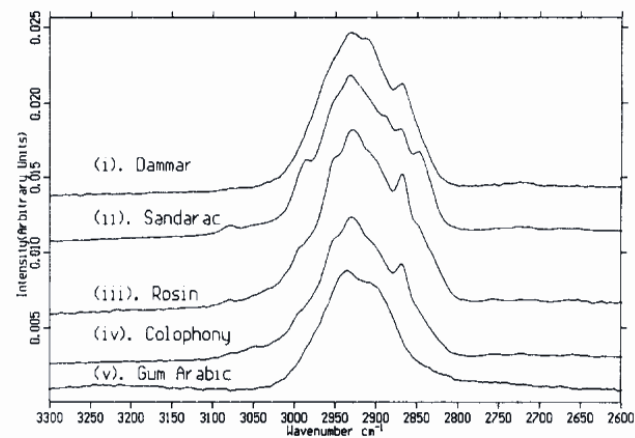


Fig. 2. FT-Raman spectra of the  $\nu(\text{CH})$  stretching region,  $2600\text{--}3300\text{ cm}^{-1}$  ( $\text{Nd}^{3+}/\text{YAG}$  laser excitation at  $1064\text{ nm}$ ; nominal laser power,  $50\text{ mW}$ ; spectral resolution,  $4\text{ cm}^{-1}$ ; 2000 scans accumulated).

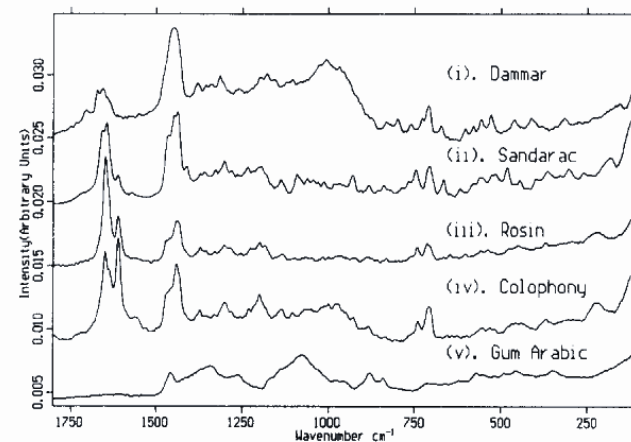
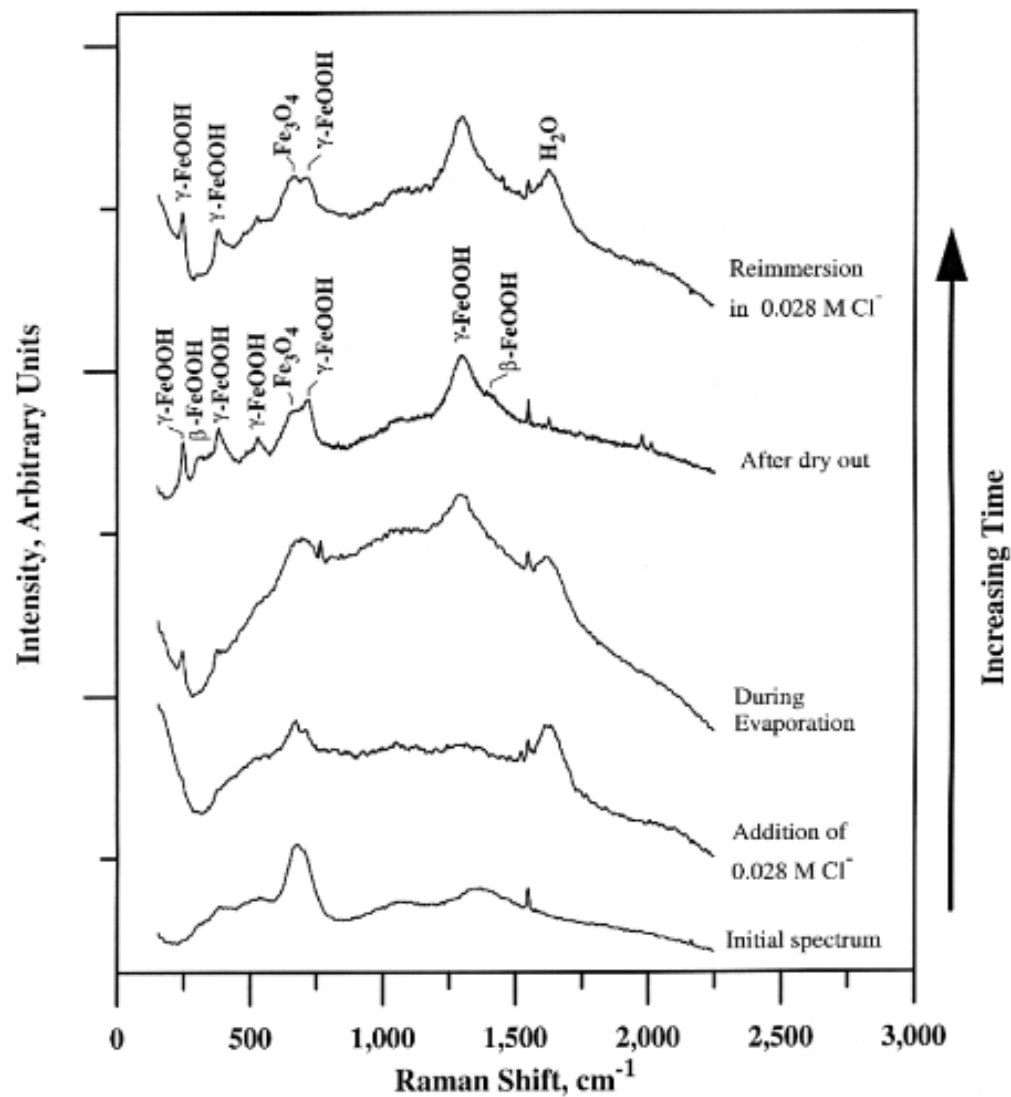


Fig. 3. FT-Raman spectra of the wavenumber region  $100\text{--}1800\text{ cm}^{-1}$ ; conditions and sample identification as for Fig. 2.

# Korozní produkty



# Identifikace textilních vláken

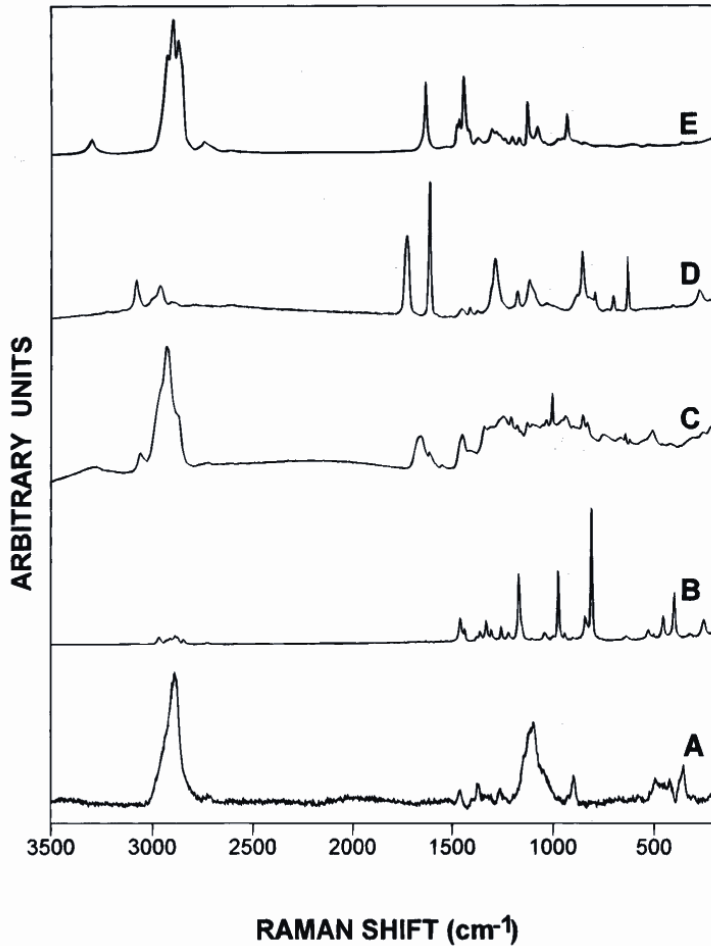


FIG. 1—Raman microprobe spectra of a range of fiber types using excitation at 632.8 nm. (A) rayon; (B) polypropylene; (C) wool; (D) polyester; (E) nylon.

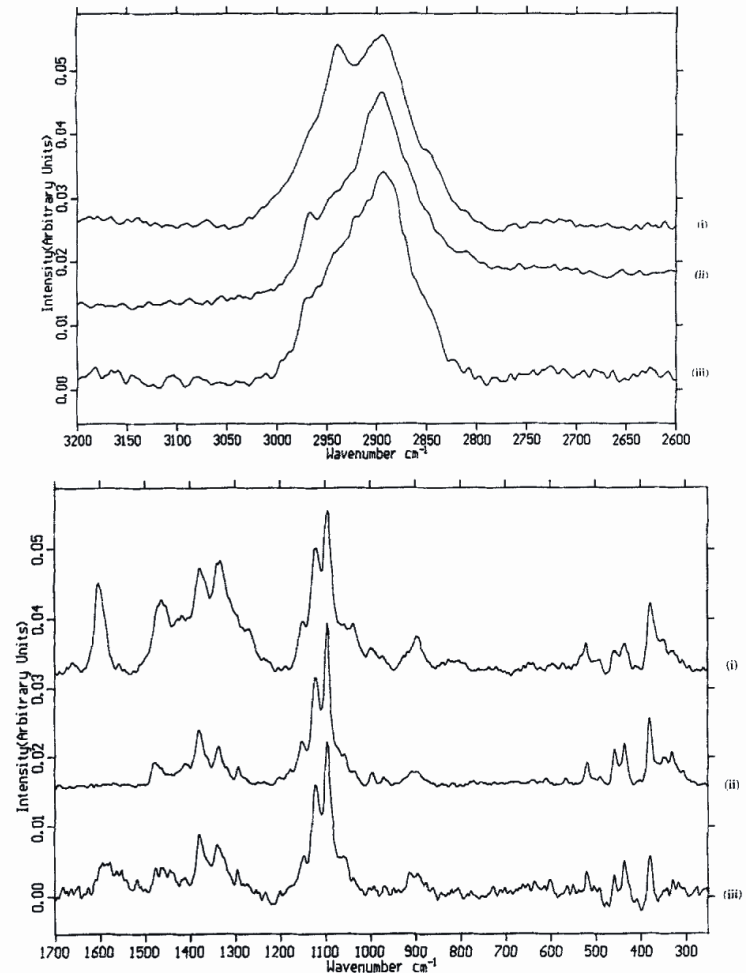


Fig. 2. FT-Raman spectra of soft bast fibres, (i) jute; (ii) ramie; and (iii) flax: (a) 2600–3200  $\text{cm}^{-1}$  region; (b) 200–1700  $\text{cm}^{-1}$  region: 1064 nm excitation, spectral resolution 4  $\text{cm}^{-1}$ , 2000 scans accumulated, laser power 40 mW.

# Degradace lněných textilií

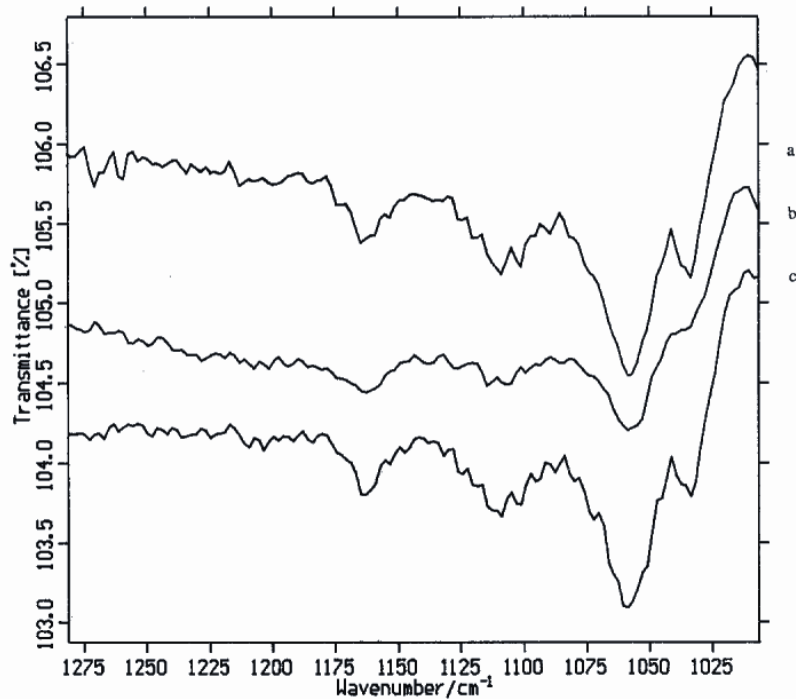


FIG. 6. Stack-plot of the infrared spectra for crystalline material (as KBr disks) from (*a* and *b*) Egyptian mummy linen samples, and (*c*) Kasr-el-Yahud linen sample; wavenumber region 1000–1280 cm<sup>-1</sup>.

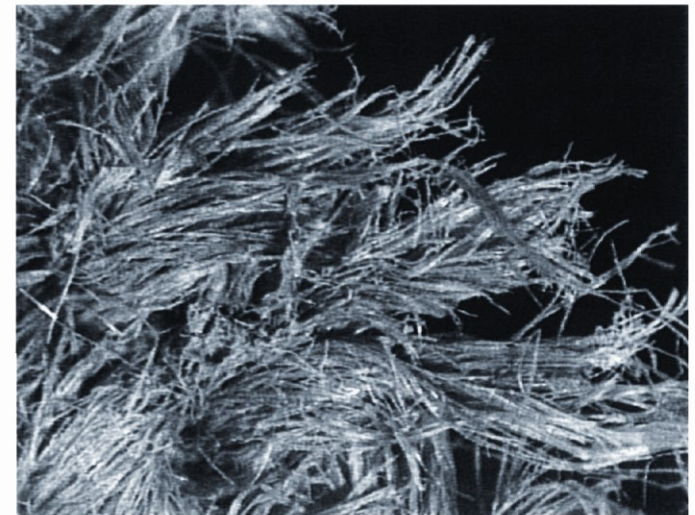


FIG. 2. Fiber damage to linen fabrics in highly colored area (enlargement 6×).

# Přítomnost mikroorganismů (lišejníky)

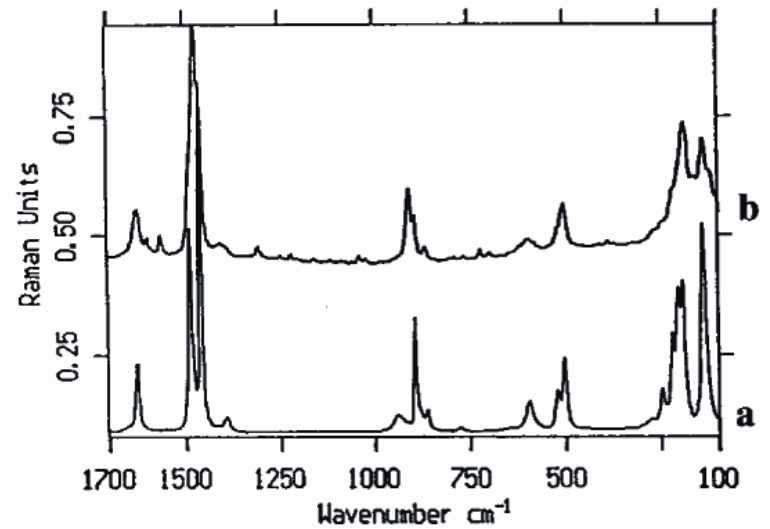


Fig. 3. FT-Raman spectra of calcium oxalate *a* monohydrate and *b* dihydrate;  $\Delta\nu = 100$  to  $1700 \text{ cm}^{-1}$ ;  $4 \text{ cm}^{-1}$  resolution;  $1064 \text{ nm}$  excitation.

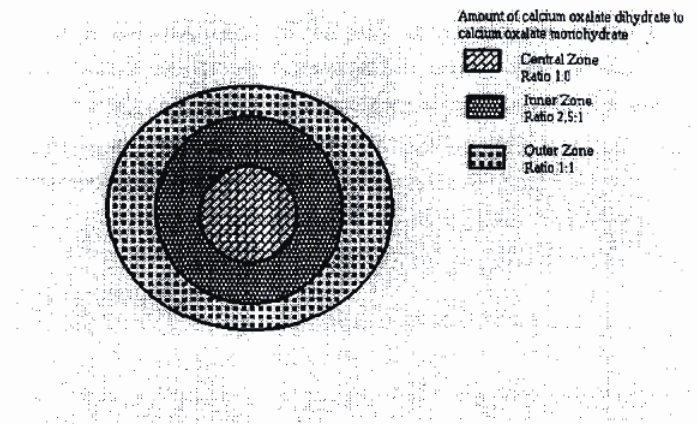


Fig. 4. Distribution of calcium oxalate monohydrate and dihydrate in encrustation of *A. oxytoma* thallus.



# Ostatní aplikace

- Pergamen
- Papír a inkoust
- Organická barviva (textilie)
- Obsidián (provenience)
- Keramika (řezy)
- Znečištění a degradace povrchu kamene

# Další metody

- LIBS
- LIF
- LIDAR
- AAS s laserovými diodami